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Examination of post-reaction residues of pyrotechnic material – p. 1: Smoke generators

Summary

The work contains a review of literature data referring to the methods of generating pyrotechnic smokes with inclusion of chemical composition of widely used smoke generating substances and, in particular, specifications of dyes used in pyrotechnic products. Construction of such devices, the manner of initiating ignition and possibilities of identification of residues resulting from their use were explained basing on 79 examined smoke generators. Analyses of smoke generating mixtures were executed with use of classical chemistry techniques, spectroscopy in infrared light (FTIR-ATR), electron microscopy (SEM-EDX), as well as gas chromatography-mass spectrometry (GC-MS). The analyses have demonstrated that 2-methylanthraquinone is most often used for generating white smokes, soot – for generating black smokes, quinolone dyes – for yellow smokes, copper phthalocyanine for blue smokes, and anthraquinone dyes for the remaining colours.

The GC-MS technique has proven an effective analytical tool both for identification of the dye in the smoke generating substance and detection on various surfaces of traces resulting from the use of smoke generator.

Key words: pyrotechnic generation of smokes, smoke generating substances, azo dyes, anthraquinone dyes, triphenylmethane dyes, diphenylmethane dyes, phthalocyanine dyes, thiazine dyes, quinoline dyes

1. Introduction

Due to the easy availability and high popularity of pyrotechnic materials they are repeatedly used for purposes other than those for which they are intended, primarily during matches or other sports events, or less frequently, e.g. to initiate a fire. The Act of 20 March 2009 on the safety of mass events, in article 59, penalizes the bringing and possession of weapons and ammunition, fire-hazardous materials or other dangerous objects, as well as pyrotechnic materials. The reality in a sports stadium, however, is that pyrotechnic materials, first of all, colour flares and smoke generators, are commonly fired during matches. Despite the existing legal prohibitions and the imposition of stadium bans, this practice is still functioning and very often the “light tifo display” gets out of control, potentially posing a threat to the health or life of the event participants. An example of such a situation is shown in Figure 1 (photo taken during the 2018 Polish Football Cup finals).

This problem is reflected by requests for expert examinations submitted to police forensic laboratories, the primary purpose of which is to link the debris of

Fig. 1. Polish Football Cup finals, 2018, The National Stadium.

Fig. 2. Debris of fired green smoke generator.

Fig. 3. Disposable protective coat with deposit of green substance.

spent pyrotechnic products detected at the scene with a specific detained person. In the case of chemical laboratories, this entails the need to perform a trace analysis of samples collected most often from suspect's clothes or hands for the presence of characteristic combustion products of pyrotechnic mixtures. An example of test material submitted to Chemistry Department in the Central Forensic Laboratory of the Police (CFLP) on a case related to the use of smoke generators is shown in Figures 2 and 3.

General information about the structure and principle of operation of pyrotechnic smoke generators and the composition of smoke mixtures are available in literature, however, chemical analysis of the combustion products of these materials, especially the organic dyes used in them, in the aspect of forensic examinations is very rarely discussed in specialist sources. There is also a lack of data on which of the large number of potential use dyes are used in practice in products currently available in the market. Therefore, a research project was undertaken in CFLP Chemistry Department, the aim of which was, among others, creating a database containing information on the structure and chemical composition of pyrotechnic materials presently available in the market, developing an analytical method for detecting traces of substances (mainly dyes) after their use, and supplementing the libraries of MS and IR spectra of relevant analytes.

2. Methods of pyrotechnic smoke generation

2.1. White smoke

The methods of pyrotechnic production of white smoke, due to the origin of the smoke generating factor, can be divided into two groups, in which:

- the smoke generating material is contained in the pyrotechnic mixture,
- the smoke generating material is formed during the combustion of this mixture.

The first group refers to substances which sublimate under the conditions of the mixture combustion and then re-sublimate to form smoke. These substances may be organic (e.g. anthracene, cinnamic acid, terephthalic acid, 2-methylanthraquinone) or inorganic (ammonium chloride) compounds. The heat necessary for the evaporation of the smoke generating substance is provided by an exothermic combustion reaction, in which the fuel may be the smoke generating substance itself (then we are dealing with the process of partial combustion and partial sublimation) or another, non-volatile component of the mixture (e.g. lactose). In practice, potassium chlorate is almost always used as an oxidant.

In the other group of the said mixtures, the smoke generating agent is an inorganic product of combustion of the pyrotechnic material. Of course, in the combustion products of virtually every pyrotechnic mixture there are inorganic compounds responsible for the generation of larger or smaller amounts of smoke, but the really high smoke efficiency is ensured by combustion products characterized by high hygroscopicity, creating a mist of water solution droplets in the air. Examples are zinc (II) chloride, formed during the combustion of mixtures based on organochlorine compounds and zinc oxide and/or metallic zinc, as well as phosphorus (V) oxide, which is the product of combustion of phosphorus-containing materials. Since, by weight, most of the smoke produced is not from the material alone, but from the atmospheric humidity, mixtures of this type are among the most efficient means of creating screen smokes. Their effectiveness is, of course, related to the relative air humidity. An example of the composition of such a mixture, which is also an interesting case of using an oxygen-free oxidant, is presented below:

- hexachloroethane – 53%,
- zinc – 44%,
- magnesium oxide – 3%.

2.2. Black smoke

Soot, produced in the process of incomplete combustion of organic fuel, is practically the only smoke generating factor of the present-day black smoke pyrotechnic mixtures. An example of a mixture of this type is presented below:

- potassium chlorate – 55%,
- anthracene – 45%.

2.3. Coloured smokes

All currently used methods of pyrotechnic generation of coloured fumes use the effect of sublimation/resublimation of organic dyes, analogous to the method presented in the description of white smokes. None of the historically proposed methods using coloured inorganic compounds introduced into the pyrotechnic mixture or generated during its combustion have given satisfactory results.

In some simplification, the composition of typical coloured smoke material can be represented as follows:

- thermal mixture – 50%,
- dye – 50%.

The term "thermal mixture" should be understood as a fuel-oxidant pyrotechnic system meeting specific operational requirements. The heat of combustion of such a system, on the one hand, must be high enough to allow the dye to sublimate and ensure the reaction self-sustaining, but on the other hand, the combustion temperature must not be too high, as this would result in thermal decomposition of the dye. The thermal mixture should also produce as many gaseous products as possible with a small amount of solid slag with a porous structure allowing free migration of dye vapours. The system most frequently suggested in the literature is potassium chlorate/lactose in a weight ratio nearly 3 to 2, although there are also reports on the use of the potassium chlorate/sulphur system. Occasionally, coloured smoke material is mixed with substances that lower the combustion temperature and increase the chemical stability of the mixture during storage, e.g. sodium bicarbonate and fillers such as talc or diatomaceous earth.

It should be emphasised that in order to obtain coloured smoke of good quality, it is necessary that the combustion of the pyrotechnic material takes place in conditions that protect against air access, i.e. inside the smoke candle body. The candle design should also ensure that the stream of combustion products is cooled sufficiently before their discharge into the surrounding air. If these conditions are not met, the dye vapours self-ignite on contact with air, resulting in loss of colour and formation of soot. This also applies to white fumes produced by sublimation of organic compounds.

3. Dyes udes in smoke generating mixtures

Before beginning to consider the requirements as regards dyes for smoke generating materials, it is worth to touch upon the issue of nomenclature. A dye can be uniquely defined using a chemical name, however the complexity of its structure makes such a nomenclature impractical, except for the simplest molecules (e.g. p-aminoazobenzene). In the literature, one can most often find customary names (e.g. quinizarin, rhodamine) or commercial names (e.g. Solvent Yellow 56, Disperse Red 9).

Customary names sometimes have an unambiguous connotation (e.g. quinizarin), but often show generic character. In such situations, additional indices point to a specific compound; for example, the names rhodamine B, rhodamine 6G, rhodamine 123 refer to three different compounds from the group of xanthene dyes. This is important because sometimes a slight modification in the dye molecule, reflected in a change in the index in the common name, makes the compound completely unsuitable for pyrotechnic smoke production. An example is quinoline yellow, which occurs in the WS (Water Soluble) and SS (Spirit Soluble) varieties, where the WS variation is distinguished by the $-SO_3Na$ group introduced into the molecule, which makes the compound water-soluble, but at the same time deprives it of the volatility necessary for thermosublimation processes of obtaining smoke. The situation is further complicated by the possible presence of certain dyes in the form of base or various salts. For example, rhodamine B is commercially available as a base or a hydrochloride, each of these forms having different properties for use in smoke-producing materials.

Commercial names of dyes usually have a three-part structure, comprising the specification of characteristics of the dyeing process in which a given substance is used (Direct, Solvent, Disperse, Acid, Reactive, etc.), the colour name and the sequential number in a given group. It should be remembered that one and the same dye may be found under different commercial names, that vary even in the colour indication, e.g. the terms Solvent Blue 90, Disperse Blue 72 and Solvent Violet 13 refer to the same substance: 1-hydroxy-4-(4-methylanilino) anthraquinone. Taking into account the above complications, in order to avoid misunderstandings, e.g. when ordering reagents, it is worth using a unique CAS (Chemical Abstract Service) or CI (Color Index) number.

The basic requirement for dyes used for coloured smokes pyrotechnic materials is the ability to sublimate at the mass combustion temperature, with the lowest possible involvement of decomposition reaction. This requirement eliminates high molecular weight dyes as well as those that are in the form of non-volatile metal salts (e.g. $R\text{-}SO_3Me$, R-OMe). By contrast, salts in which the dye is in cation form may produce good quality smoke (e.g. rhodamine B, methylene blue).

Some sublimable dyes are highly susceptible to oxidation or catalytic decomposition in contact with hot solid combustion products of the pyrotechnic mixture. In such cases, good quality smoke can only be obtained if the smoke generator is designed to quickly evaporate and cool the dye vapours, with a minimum contact time with hot cinder. This is achieved by giving the pyrotechnic material a granular form or a cylindrical shape with an axially drilled hole and the use of heat sinking elements, such as metal mesh or perforated sleeves.

Another requirement for the dyes of smoke generating materials is compatibility with other components of the mixture. Since pyrotechnic mixtures based on potassium chlorate are unstable in presence of acids, acidic dyes are used only with the simultaneous incorporation of alkalizing substances, e.g. carbonates in the material. This remark refers to, e.g. rhodamine B hydrochloride, the aqueous solution of which has a pH value in the range of 2 ÷ 3. A tendency to spontaneous exothermic reactions in the presence of moisture, potentially resulting in spontaneous combustion of the material, was also observed for mixtures containing auramine O, in which the thermal effect was attributed to an undefined reaction between auramine and lactose (Henry, Eppig, 1945).

Further restrictions are imposed by the requirement of the lowest possible toxicity of produced smoke. Over the years, a gradual increase in awareness of the risks in this area have been observed resulting in the withdrawal of certain dyes, e.g. benzanthrone or Vat Yellow 4. from the use of old publications. One can be astonished, indeed, by descriptions of smoke-producing materials based on such highly toxic substances as arsenic sulphide or cadmium sulphide, as presented in publications from old times.

The number of dyes that have been synthesized so far is so large that, even after taking into account the above limitations, many substances potentially useful for pyrotechnic smoke generation remain. Table 1 lists the dyes proposed for this purpose in the literature. For the sake of clarity they are divided into classes basing on chemical structures.

Among the substances mentioned attention ought to be given to copper phthalocyanine, which due to its insolubility in all common solvents should be classified as a pigment rather than a dye. It is the only organic compound used in pyrotechnics to colour smoke that contains a metal (Cu) atom. Some smoke generating material formulas contain two dyes. This is most often the case in green smokes, obtained from a combination of blue and yellow dyes, as well as purple smokes, created from a combination of blue and red.

4. Analysis of pyrotechnica materials market

The Authors were mainly interested in such smoke generators which, according to the instructions for use, allowed holding the devices in hands while firing, or provided such a technical possibility. There is a large number of shops and wholesalers on the Polish market that trade in pyrotechnics. After reviewing the generally available offer, the bidder who guaranteed the greatest variety of assortment was selected. Due to the rather enigmatic trade names, it was not possible to verify before making a purchase whether all of the purchased items met the criterion of “misuse” potential. In order to group and classify the obtained pyrotechnic materials, as well as for the subsequent collection and processing of information, an IT tool was developed in the form of a database of tested products.

The gathered pyrotechnic materials were divided into the following groups: flares, signal flares, strobes, smoke generators, pyrotechnic fountains, pyrotechnic torches and flash crackers. Some of the materials made up sets with different colour effects, and in those cases each element that differed in colour was treated as a separate item. Each of the specimens was subjected to macroscopic tests, during which, first of all, the appearance of the product was recorded in the form of photos, so that it was possible to read information on the use, net mass of the explosive (NEC) and the chemical composition, as declared by the manufacturer.

Following registration in the database, the products were subjected to macroscopic tests, which included analyses of the product characteristics and determination of ignition initiation method. After breaking the products apart the pyrotechnic material was weighed and its samples were taken for further instrumental tests to determine its chemical composition. 79 different smoke generators were selected for the tests, an example of the product’s appearance is shown in Figure 4.

5. Construction of smoke generator

Most of the tested smoke generators contained smoke generating mixture in a form of a cylindrical charge in a cardboard casing, closed with a cork made of mineral material with an axially drilled hole allowing the mixture to ignite and the combustion products to be released. Larger generators had cardboard shutters with several holes, sometimes located on both sides of the product. The consistency of the mixtures ranged from loose material contained in foil packets, to highly compressed, typical for products of the largest weight (in this case, the molding usually additionally had a longitudinal, axial hole). The actual amounts of pyrotechnic materials in the tested products ranged from 6.9 g to 394 g and was usually lower than the NEC value provided by the manufacturer, ranging from 10 g to 450 g.

The ignition mechanism of the products was most often in the form of a short section of a Visco fuse or a friction igniter with a strike strip, less often a friction igniter with a wire or string. Against this background, two among the tested product types stood out. The first one, shown in Figure 5, contained piezoelectric igniter made of an electric pulse generator, similar in appearance and operation principle to generators commonly found in gas lighters, connected to copper insulated wires ended with an igniter head. The head itself was a rather unusual construction, because it was bridgeless and, upon removal of the pyrotechnic material, it was reduced to a pair of twisted, perpendicularly cut wires.

The igniting charge of the head was based on a mixture of lead (IV) oxide with silicon. The second, original type of smoke generator was styled as a hand grenade and had an igniter controlled by a trigger lever (Fig. 6). The ignition mechanism was activated by releasing a spring-driven plastic trigger, locked in the transport position with a cotter pin with a pulley. Unlike in typical hand grenades, the trigger did not cooperate with the firing pin, but it was connected with the steel wire of the friction igniter. The lever's powerful spring and its large stroke provided an effect analogous to the vigorous jerking of the igniter pulley by hand.

6. Analysis of smoke generating materials and their combustion traces

Analyses of the chemical composition of smoke generating pyrotechnic mixtures were carried out using the Fourier transform infrared spectroscopy with the method of attenuated total reflectance (FTIR-ATR), electron microscopy with an X-ray energy dispersion

Table 1. List of dyes used, according to the literature, in production of smoke generating mixtures.

Colours	**Dyes**							
	azo	**anthraquinone**	**triphenylmethane**	**diphenylmethane**	**nitro dyes**	**phthalocyanine**	**thiazine**	**quinoline**
Yellow	p-aminoazobenzene	Vat Yellow 4, CI 59100		auramine O, CI 41000	p-nitroaniline			quinoline, yellow CI 47000
	Solvent Yellow 56 (N,N-diethyloaminoazobenzene), CI 11021	alizarin						
Red	paranitroaniline red (Pigment Red 1), CI 12070	Disperse Red 11, CI 62015	rhodamine B – compound from xanthene dye subgroup, CI 45170					
	Sudan Red G (Solvent Red 1), CI 12150							
	Oil Red O (Solvent Red 27), CI 26125	Disperse Red 9 (1-metyloaminoanthraquinone), CI 60505						
Green		Solvent Green 3, CI 61565	malachite green					
Blue		Solvent Blue 36, CI 61551	Victoria Blue BO (Solvent Blue 5), CI 42595:1			copper phthalocyanine, CI 74160	methylene blue	
		Oil Blue 35, CI 61554						
		Disperse Blue 14, CI 61500						
Brown	chrysoidine							
Violet		Solvent Violet 13, CI 60725	crystal violet					
		Solvent Violet 47, CI 61690						
Orange	Sudan I (Solvent Yellow 14), CI 26000	quinizarin						

spectrometer (SEM-EDX) and gas chromatography/ mass spectrometry (GC-MS). The latter technique was found to be particularly useful for the identification and detection of organic dyes capable of sublimating at elevated temperature.

The research included not only samples taken from the generators, but also traces of their use collected during field tests. Field tests were carried out by firing up the smoke generating devices in accordance with the appended manufacturers' operating instructions. During combustion, the devices lay on the ground or were held in the hand of the operator, if their instructions for use allowed it. In the case of products burnt on the ground samples for laboratory tests were collected on pieces of white cotton fabric of 100 cm^2 surface by immersing the fabric in a stream of smoke at a distance of several centimetres from the outlet for a few seconds. An example of a sampling operation is shown in Figure 7.

In the case of hand-held candles, the operator's outerwear was secured for further tests. Samples recovered on fabric or clothing cuttings were packed in polyethylene zipper bags. In order to prepare analytical samples for GC-MS analyses, fabric cuttings or soiled areas of clothing were extracted with chloroform under laboratory conditions.

During the polygon tests, sporadic faults in the operation of the generators were observed, such as inflammation of the smoke stream or failure of friction igniters (breaking of rods, bending of pulleys). In the case of the white smoke generator labelled "TXF 651", firing attempts each time ended in a violent explosion combined with breaking of the cardboard body of the device. The likely cause of that can be found in the specific composition of the smoke mixture: hexachloroethane, a substance of high volatility, was used as the smoke generating agent; the cardboard body of the product

Fig. 4. Generator of blue smoke with a fuse initiating system.

Fig. 5. Smoke generator with a piezoelectric ignition system.

Fig. 6. Smoke generator with a friction igniting system and a trigger lever.

Fig. 7. Collection of analytical sample from a stream of smoke.

did not provide sufficient protection against sublimation of hexachloroethane, so with passing time the smoke generating mixture might have changed its composition, transforming into a mixture of potassium chlorate, starch and sulphur with clearly marked explosive properties. Regardless of the cause, the effect is instructive; it reminds that smoke generating mixtures are, like all other pyrotechnic mixtures, a variation of explosives, and even seemingly harmless products such as smoke candles may, in certain situations, pose a threat to the user's health.

6.1. SEM-EDX

Electron microscopy coupled with energy dispersive X-ray detection (SEM-EDX) turned out to be a useful tool for the identification of inorganic components of pyrotechnic materials, allowing recognition or confirmation of the presence of additives whose function is to regulate the dynamics of combustion and dispersion of combustion products. They include: sodium carbonate, calcium and magnesium carbonate, silica, barium sulphate, and aluminosilicates. The oxidizing agent, potassium chlorate, is also easily recognizable.

Organic dyes commonly used in generators were visible in the microscopic image, however, their humble elemental composition, which in the X-ray spectrum manifested only oxygen, carbon, nitrogen and chlorine signals did not provide give any discriminatory information either before or after firing the smoke generators. The only exception was copper phthalocyanine, which is the source of signal from copper. The percentage of copper in the mixture is, however, too small to use it as a marker and to enable searching for possible traces of copper on the clothing and bodies of the perpetrators.

The examinations were carried out on the Tescan Mira 3 LMU electron microscope coupled with the X-MaxN SDD X-MaxN energy dispersion spectrometer by Oxford Instruments in conditions typical for microanalysis of traces. Prior the analyses representative samples of pyrotechnic materials transferred to stubs surfaces were vacuum coated with carbon in a standard manner, and then analysed using a BSE detector, which enabled classification of heterogeneous mixtures on the surface of the table in terms of their average atomic masses. Spectra were recorded from selected spots differing in atomic masses. The spectra were analysed in terms of the possibility of assigning them to specific chemical compounds on the basis of the intensity of individual spectral lines, which made it possible to calculate mass fractions of the elements. Of course, this was not possible with organic compounds, such as e.g. starch, lactose or organic dyes. An exemplary image of the smoke mass is shown in Figure 8. The analysis of the spectra made it possible to confirm that the components of this sample taken from the blue smoke generator were: potassium chlorate, barium sulphate, and traces of copper indicated the presence of copper phthalocyanine (Fig. 9).

Additionally, different shades of grey of substances present on the surface of the microscope stage indicated the presence of at least three different chemical compounds.

6.2. FTIR-ATR

The FTIR-ATR method was used to identify both the actual smoke generating substances and other components of smoke generating materials. In order to obtain less complex spectra that would be easier to analyse prior to tests a dye was usually separated from the rest of the sample components by chloroform extraction.

Perkin Elmer Spectrum Two spectrophotometer with an ATR accessory was used for the analysis. First, spectra of the purchased twenty pure organic dyes selected on the basis of the literature as the most likely to be encountered in smoke generating materials were recorded. A representative sample of the smoke generating material was collected from each of the

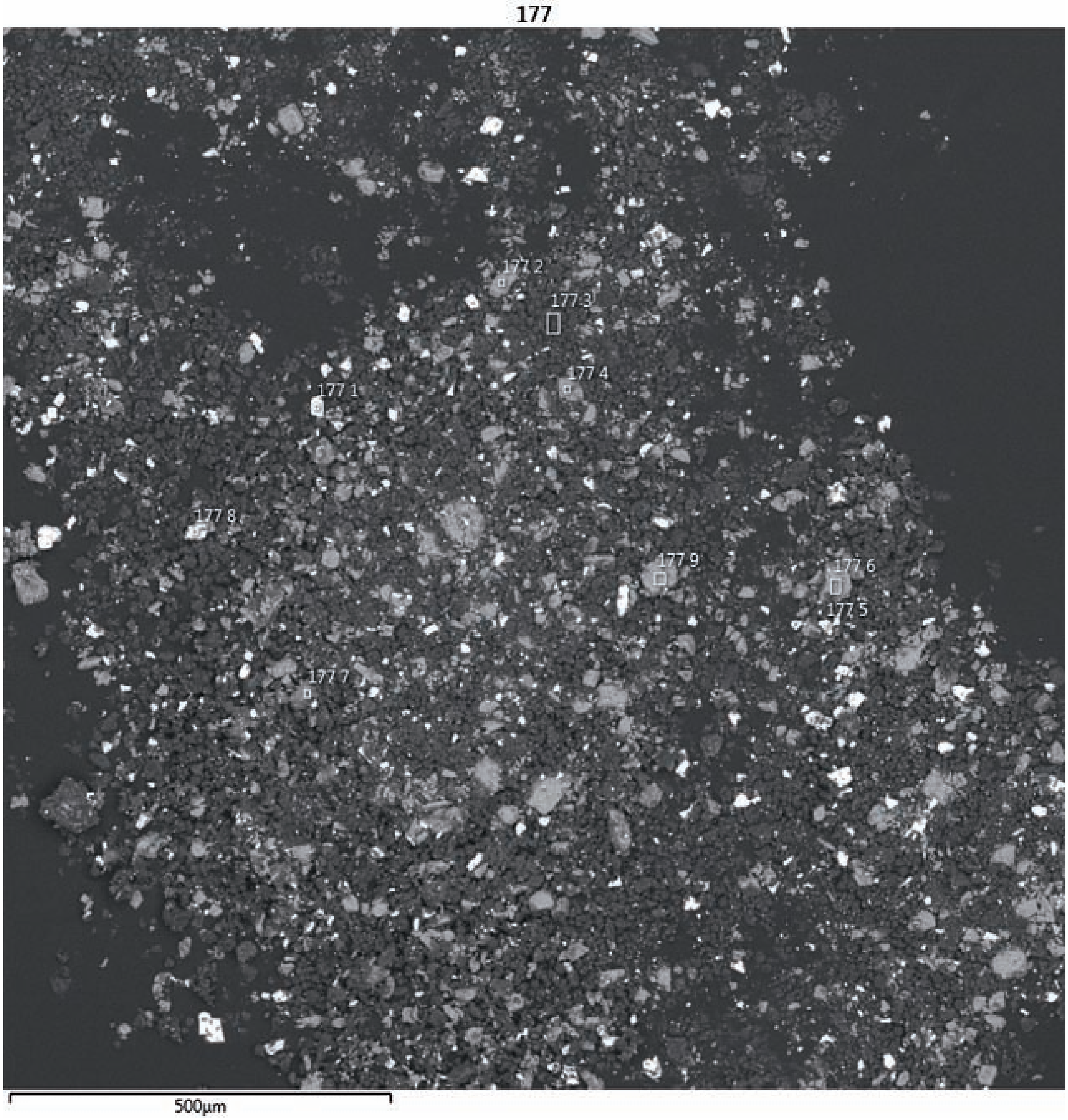

Fig. 8. Microscope image of smoke generating material based on copper phthalocyanine.

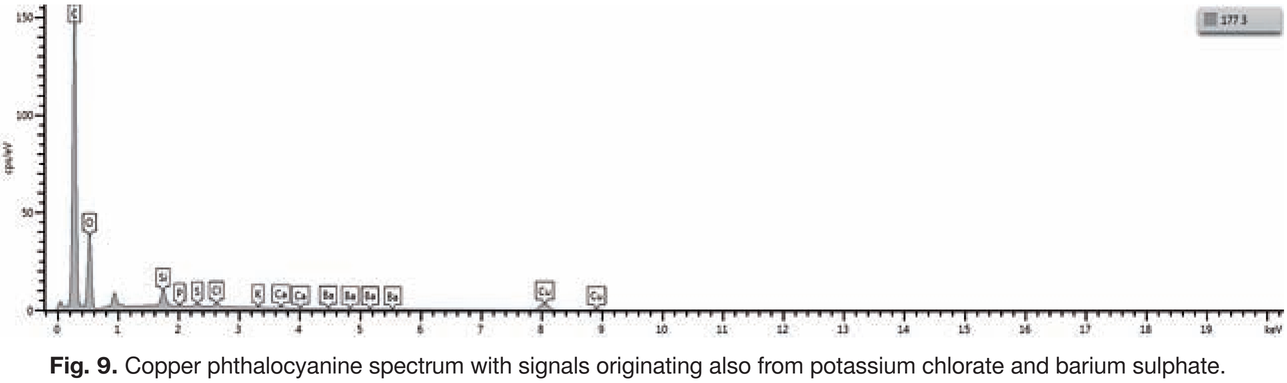

Fig. 9. Copper phthalocyanine spectrum with signals originating also from potassium chlorate and barium sulphate.

generators, and subsequently analysed after due preparation (separation, homogenization).

In addition to the identification of dyes, the method used allowed detecting the oxidant (potassium chlorate (V)), organic fuels and some additives. As an example, Figure 10 shows a spectrum of yellow smoke generating material.

6.3. GC-MS

Preliminary trials using GC-MS have demonstrated that many dyes are characterised by a strong retention on standard Rtx-5 low-polar phase columns and, therefore, their effective analysis requires short columns and high temperature conditions. At the same time, smoke generating materials may contain substances of relatively high volatility, not necessarily dyes (e.g. hexachloroethane), which should also be included in the detection capability. Taking into account the above issues, the analytical method was selected with the parameters, as follows:

- chromatograph: TraceGC 2000 Thermo Quest,
- dispenser: 250°C, *split* mode 1:80 or *splitless* mode with 1 min dispensing time (for trace analyses),
- injection: 1 µl, TriPlus autosampler, *hot needle* technique,
- column: Rtx-5ms, length 15 m, internal diameter 0,25 mm, 0,25 µm film,
- carrier gas: He, 1,5 ml/min,
- temperature program: isotherm 45°C/1 min, ramp 25°C/min do 290°C, isotherm 290°C/25 min (total time: 38,27 min),
- spectrometer: PolarisQ Finnigan (ion trap), EI ionization, scanning in the range of 29–600 m/z, 1 min solvent delay; single scan time 0.39 s.

In the first phase of the analysis, a number of reference substances, i.e. purchased dyes, mostly in form of chloroform solutions were analysed. Identification of detected compounds was performed with use of the NIST02 library and basing on the retention times and spectra recorded for reference materials. Methylene blue, auramine O, rhodamine B and Victoria Blue BO used as reference materials had a form of chlorides, while malachite green was in oxalate.

Next, samples collected from commercial smoke generators were tested, also in form of chloroform extracts. Dyes detected in the materials of the examined smoke generators, with no reference material or library spectrum available, were identified by mass spectrum interpretation, the result of which was verified with X-ray diffractometry, following separation of the dye from the remaining components of the pyrotechnic materials.

An exemplary result of the GC-MS analysis of the smoke generating material is presented in Figure 11, while Table 2 contains the basic results of the GC-MS tests for components detected in the purchased smoke generators or potentially present in the smoke generating mixtures. The first five lines of the Table contain substances used as white smoke generating agents or fuels, and there are dyes in the remaining line.

The analyses of all the substances in the table under the applied conditions of the method succeeded, except for copper phthalocyanine, for whom there is no solvent suitable for the GC technique (this substance is soluble in concentrated sulphuric acid), although few of the dyes are actually susceptible to thermal decomposition under the conditions of the analysis.

Triphenylmethane dyes (malachite green, Victoria Blue BO) and methylene blue, belonging to the group of thiazine dyes, are registered as non-ionic reduced *leuco* forms. It is worth noting at this point that triphenylmethane dyes in a strongly alkaline environment transform into a carbinol form (with a –OH group on methane carbon), which may give a separate chromatographic band in analysis of extracts from alkaline aqueous solutions. Figure 12 presents the structures of the mentioned forms based on the example of malachite green, accompanied by the results of GC-MS analysis of the alkaline chloroform extract of this dye.

Solvent Violet 47 (1,4-diamino-2,3-dihydroanthraquinone) gives a chromatographic peak with a spectrum consistent with that of 1,4-diaminoanthraquinone (Solvent Violet 11), which indicates its thermal dehydrogenation. According to the literature, such a reaction may occur even under relatively mild conditions (Patent US3433811A).

Besides methylene blue, which is well-soluble in methanol, all the tested substances dissolve efficiently in chloroform thus meeting GC-MS requirements. As regards solubility a peculiar situation was observed in the case of Disperse Yellow 54 quinoline dye. The analytical standard of this substance (Aldrich, cat no. S480037-25MG) was characterised, contrary to the dye extracted from the smoke generating material, by poor solubility in organic solvents as well as a distinct difference of IR spectrum. The GC/MS analysis, however, did not demonstrate any differences in the retention time or mass spectrum between these substances. Moreover, it was observed that the standard was easily extracted to chloroform from hydrochloric acid environment, whereas the chloroform evaporation residue yields IR spectrum corresponding to the dye from smoke candles. As several isomeric structures can be developed for Disperse Yellow 54 (Fig. 13), it cannot be excluded that the observed effects are resulting from keto-enol or imine-enamine tautomerism.

For a few selected substances (2-methylanthraquinone, quinoline yellow, Disperse Red 9, Solvent Green 3), the limit of detection for the method in *splitless* mode was set by performing a series of analyses of chloroform solutions prepared by successive stock dilutions with the concentration of 1 mg/ml. The limit of detection (LOD) was calculated by means of the ion current chromatogram recorded for the sample of the lowest concentration producing a visible signal. To this end, chromatographic bands were automatically integrated using the Genesis algorithm in the Xcalibur software, a displayed signal-to-noise (S/N) ratio was recorded and, subsequently, the LOD value was determined based on a relation formula as the concentration of the substance at S/N = 3.

Additionally, the limit of detection for mentioned above three dyes was determined with visual method, i.e. the minimum concentration allowing for the chloroform solution of the substance to have a visible colour when placed in a glass SV-10 vial. Such a limit, determined subjectively, is of indicative value, however it allows to explain an interesting issue, namely whether the developed instrumental method can surpass human eye in terms of sensitivity, in case of dyes.

The limits of detection of GC/MS splitless mode method, determined for four selected smoke generating substances, as well as the indicative threshold of concentration, for which the chloroform solution of the substance in SV-10 vial is still characterised by the colour visible for human eye, have been presented in Table 3. For Solvent Green 3 dye, due to widely stretching chromatographic bands, which are not subject to automatic integration, the approximate value of LOD was provided.

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The results presented in Table 3 demonstrate that the Limit of Detection of smoke generating substances for GC/MS method may vary in a wide range; for the investigated substances three orders of magnitude have been observed. For the substances with high retention times, such as Solvent Green 3, due to diffusion-like stretching of chromatographic bands, a particularly poor detectability (i.e. high values of LOD) should be expected. An interesting observation is associated with the high variability in the instrumental detection vs. visual detection ratio. In case of coloured substances, the GC/MS method may prove comparable in the range of 1–2 orders of magnitude.

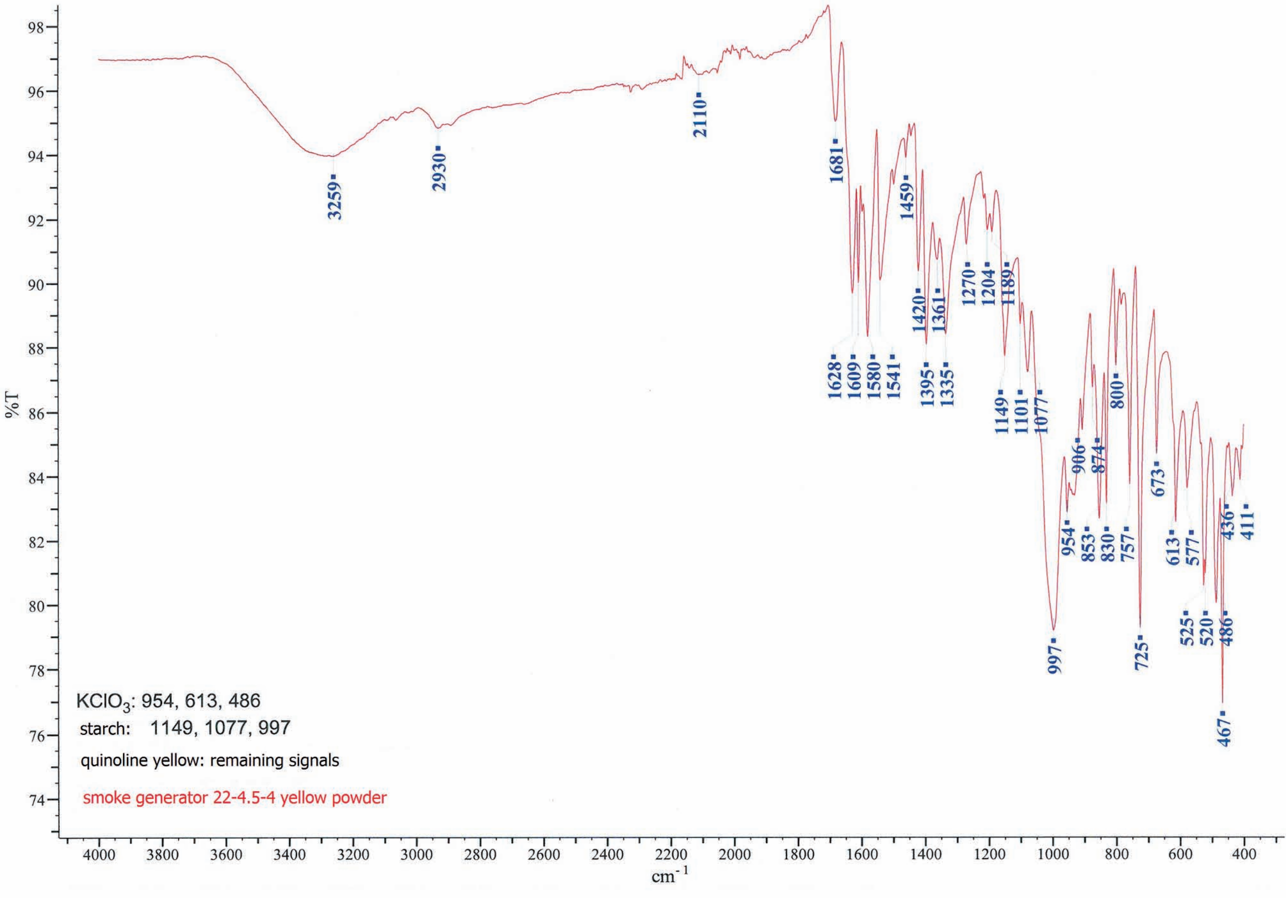

Fig. 10. IR spectrum (FTIR-ATR) of a material sample from yellow smoke generator.

7. Analytical results – summary

The results of qualitative analysis of smoke generating materials used in smoke generators commercially available at present, as well as the analysis of post-use traces allow to formulate the following observations:

1. The smoke generating substances used are based exclusively on potassium chlorate (V) as an oxidant, whereas starch and sulphur prevail as fuel. The presence of lactose was detected only in five out of seventy nine investigated mixtures.
2. The most commonly used smoke generating substances are, as follows:
   - 2-methylanthraquinone of white smoke,
   - soot as the product of incomplete combustion of organic fuel, mostly anthracene, of black smoke,
   - quinoline dyes (Disperse Yellow 54, quinoline yellow) of yellow smoke,
   - copper phthalocyanine of blue smoke,
   - anthraquinone dyes of other colours.

   Occasionally, yellow or red azo dyes can be encountered, in addition to auramine O and rhodamine B (these two substances are found in hardly water-soluble, alkaline form). Structural formulas of the most common substances are presented in Figure 14.
3. The GC/MS method is an effective analytical tool both for identifying the dye for the smoke generating substance and for detecting its traces on various surfaces as the result of the use of smoke generator. Copper phthalocyanine, used in blue fumes, constitutes the only exception, i.e. cannot be identified by GC/MS. It should be noted that the limit of detection of GC/MS method for some dyes may be inferior than it is in the case of visual method.
4. Other analytical techniques, such as SEM-EDX, FTIR or XRD are useful in the identification of pyrotechnic substances, however their potential application in detection of traces after the use of smoke generator is limited to heavily soiled surfaces or the samples taken from a burned device.
5. In the process of combustion of smoke generating pyrotechnic mixture, a certain amount of dye undergoes thermal decomposition. In particular, this concerns azo dyes and triphenylmethane dyes. Benzonitrile and phthalonitrile for copper phthalocyanine as well as quinoline, methylquinoline and phthalic anhydride for quinoline yellow are examples of the products of such decomposition. On the other hand, the concentrations of decomposition products are quite low, and therefore they are insignificant in the context of forensic examinations.

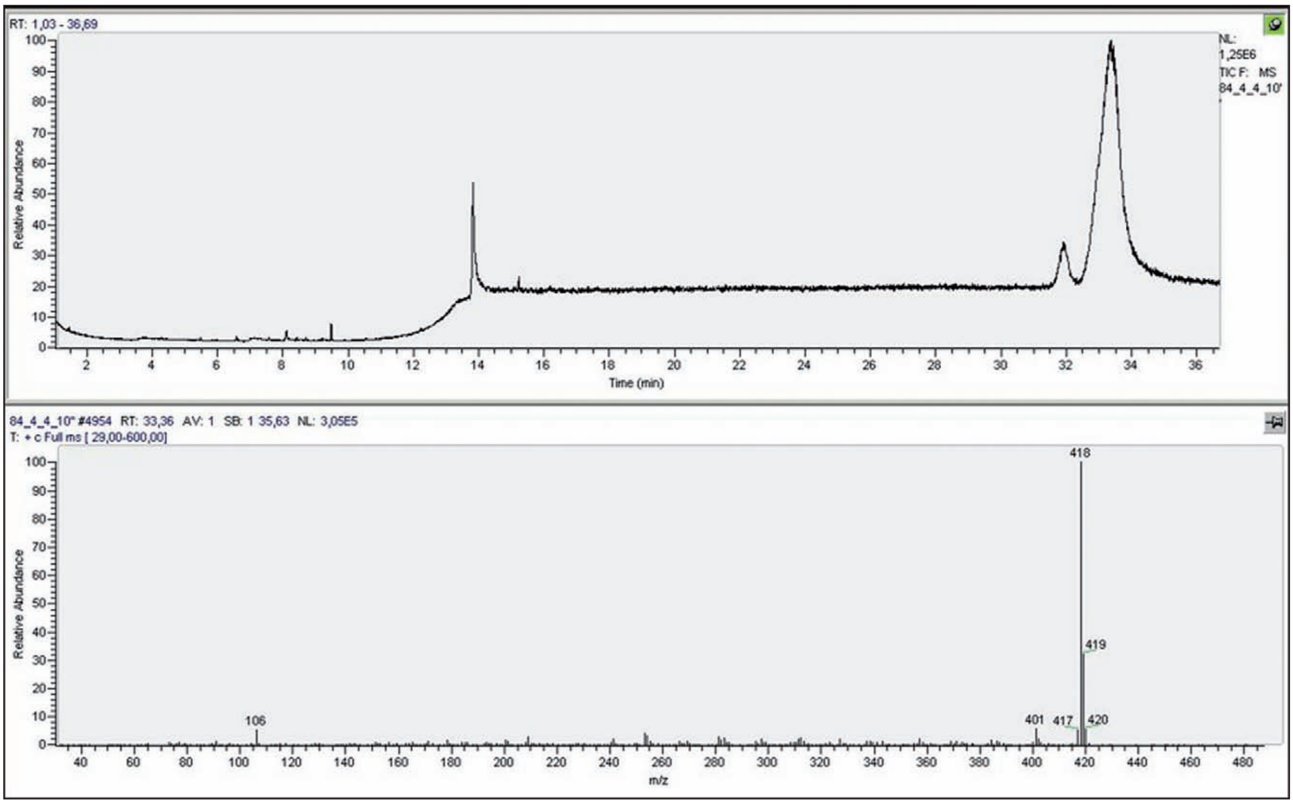

Fig. 11. Result of GC-MS analysis of $CHCl_3$ extract from green smoke generating material. Visible signals from Disperse Yellow 54 dye in 13,8 min, as well Solvent Green 3 in 31,5 and 33,3 min; bottom spectrogram – mass spectrum of Solvent Green 3 dye.

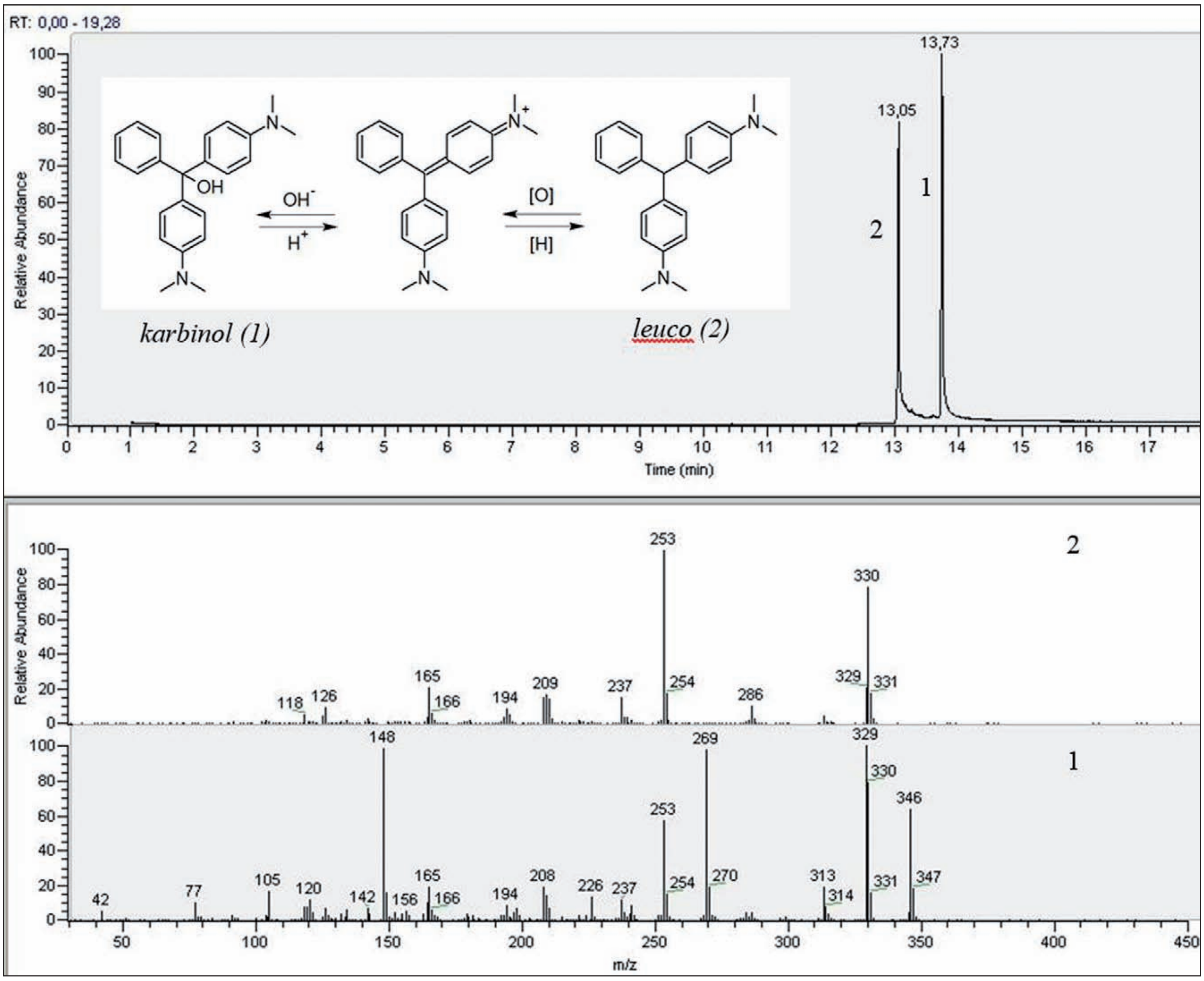

Fig. 12. Result of the analysis of a chloroform extract from an alkaline solution of malachite green. Visible bands from carbinol (1) and *leuco* (2) forms of the dye.

8. Conclusions

The presented examination results demonstrate that the analytical techniques commonly used in chemical sections of police forensic laboratories, such as GC/MS and FTIR, are potentially effective for identification and detection of dyes and other substances used in commercial pyrotechnic smoke generators.

The results of the project can be utilized not only in the field of "sport stadium pyrotechnics", but also in the examination of other forensic traces, with an organic dye as a significant component. The example may be the residues after the use of bank anti-theft devices, which use pyrotechnic smoke generators. Figure 15 shows banknotes, which were permanently stained by such a device and consequently subject to examination at the CFLP Chemistry Department.

It should be kept in mind that due to the group character of comparative chemical examinations and a wide availability of smoke generating pyrotechnic products, the detection of residues of the one and the

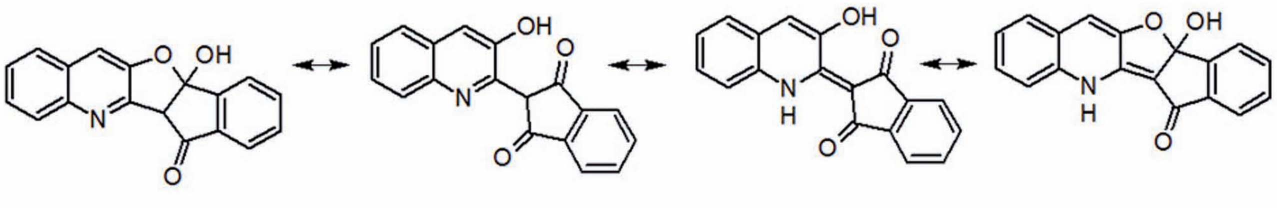

Fig. 13. Hypothetical tautomeric forms of Disperse Yellow 54.

Table 2. Results of GC-MS analyses of substances potentially encountered in smoke generating mixtures depots.

Name	Retention time /min	Spectrum base / molecular/most intense ion	Identification method/comments [d]
hexachloroethane	3.63	201	NIST, r.m./+
urotropine	4.77	140 [a]	NIST, r.m./+
anthracene	8.26	178 [a]	NIST, r.m./+
sulphur	9.51	160	NIST, r.m./+
2-methyloantraquinone	9.81	222 [a]	NIST, r.m./+
quinizarin	10.23	240 [a]	NIST, r.m./+
Solvent Yellow 56	10.96	253 [a]	r.m./+
Disperse Red 9	11.12	220	r.m./+
Sudan I	11.32	248 [a]	NIST, r.m./+
Solvent Violet 47	12.38 (decomposition product)	238 [a, c]	NIST, r.m./decomposition in analytical conditions
auramine O	12.42	223	r.m./+
Sudan Red G	12.43	278 [a]	r.m./+
Disperse Blue 14	12.94	266 [a]	NIST, r.m.
malachite green	13.05	253 [b]	NIST, r.m.
methylene blue	13.37	285 [a, b]	r.m./solution in MeOH, +
quinoline yellow SS	13.79	273 [a]	NIST, r.m./+
Disperse Yellow 54	13.83	245	r.m./refers to soluble isomer, +
Solvent Blue 90	14.50	329 [a]	MS spectrum analysis, XRD/+
Sudan Blue II	15.01	307	r.m./+
rhodamine B	22.00	326	NIST, r.m./+
Victoria Blue BO	24.42	479 [a, b]	r.m..
Solvent Blue 104	27.37 (weak) 28.26 (strong)	474 [a]	MS spectrum analysis, XRD/+
Solvent Green 3	31.55 (weak) 33.27 (strong)	418 [a]	r.m./+
Oil Red O	20.43–27.00 (several bands, strongerst: 20.43)	380 (20,43 min), 408 [a] (27 min)	r.m./decomposition of dye in analytical conditions
copper phthalocyanine	-	-	lack of solvent to enable GC analysis, +

[a] molecular ion

[b] *leuco* form

[c] 1,4-diaminoanthraquinone

[d] "r.m." – reference material, „+" – the substance was detected in at least one of the examined products.

Table 3. The limits of detection for selected smoke generating substances.

Smoke generating substance	Calculated LOD value	Threshold concentration visible to human eye
Disperse Red 9	6.3 ng/ml	~ 500 ng/ml
quinoline yellow SS	880 ng/ml	~ 300 ng/ml
2-methylanthraquinone	6.8 ng/ml	colourless solution
Solvent Green 3	5000–10 000 ng/ml	~ 500 ng/ml

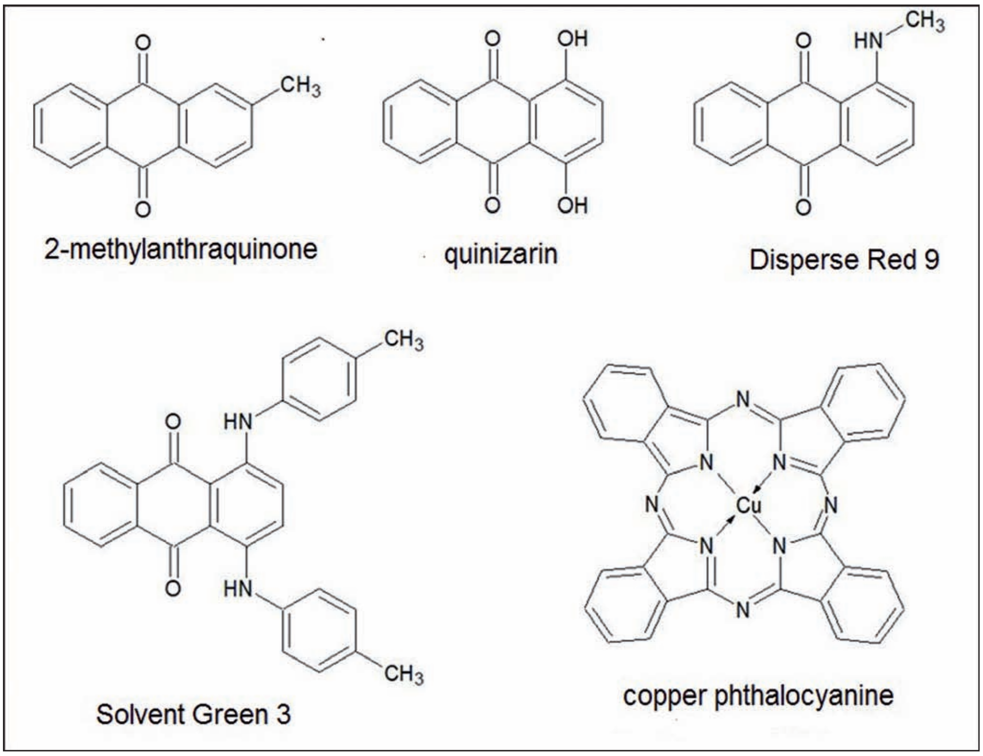

Fig. 14. Structures of common smoke generating substances used in commercially available smoke generators.

same dye, for instance on person's recovered clothes and in the burnt product collected at the scene, does not categorically link a person to the item. Furthermore, when looking briefly at Figure 1, it can be realised that the use of smoke generator at the mass event may leave traces of smoke generating material not only on the offender. In case of arising doubts or questions in this respect the use of fingerprint identification or biological analyses results may prove indispensable.

Fig. 15. Banknotes damages by smoke generator of the anti-theft device (dye used: quinizarine).

Sources of Figures and Tables:
Figure 1: https://warszawa.wyborcza.pl/warszawa/7,54420,23371995,jest-sledztwo-prokuratury-w-sprawie-zadymy-na-stadionie-narodowym.html (accessed on: 14.09.2020)
Figures 2–15: Authors
Tables 1–3: Authors

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