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Identification of Match Head Residues in Post-Explosion Debris

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ABSTRACT: A method is described to detect and identify match head residues in post-explosion debris of improvised explosive devices. The method consists of visual microscopic examination, scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS), and spot tests for elemental sulfur and chlorate ion. The technique was applied in 13 cases of exploded pipe bombs devices. In 10 of them, match head residues were detected and identified.

KEYWORDS: criminalistics, explosives, matches, match head residues

In Israel, many explosive devices used in terrorist activities consist of match heads, alone or in mixtures with other components, which are placed in pipes to form pipe bombs.

The methods for the identification of inorganic components of unreacted explosive mixtures described in the literature include X-ray fluorescence (XRF) [1], infrared spectroscopy (IR) [1], chemical spot tests [1], X-ray diffraction (XRD) [1,2,3] and ion chromatography [4]. A scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS) method was described for detection and identification of burnt match heads [5]. These numerous publications dealing with the analysis of explosives in post-blast debris do not implicitly describe methods to detect and identify match head residues.

Here, we will describe the combination of optical microscopy, SEM/EDS, and spot tests for the detection and identification of match heads in post-explosion debris. Although the only manufacturer of matches in Israel is the NUR match factory and there is no regular import of matches to Israel, 18 brands of matches from other countries were also examined (Table 1) to show the general applicability of the method. According to information that we have, when preparing an improvised explosive device, the match heads are scraped off from their wood or paper bases. Most of the constituents of the match heads are compounds of inorganic origin [5,6].

Experimental Procedure

Match head samples were examined with a stereomicroscope and by SEM/EDS (CamScan 3 SEM combined with a Tracor TN 5400 EDS system or CamScan 4 combined with a

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TABLE 1—SEM/EDS analysis of match heads.

Sample	Country of Origin	Color	Elemental Composition ^a
1	USA	white	Cl, K > S, Si > Ca, Ti, Mn, Zn
2	USA	white	Cl, K > Si, S > Mn (Ti)
3	USA	pink	Cl, K > Si, Zn > Al, S > (Ti), (Mn)
4	USA	red	Cl, K > Si, S > Zn > (Cr), (Al), (Fe)
5	USA	white	Cl, K, Si > S, Ti, Zn > Al, Ca > (Mg), (Fe)
6	USA	white	Cl, K, Si > S, Ti > (Fe)
7	USA	white	Cl, K, Si > S, Ti > Zn > (Fe)
8	USA	white	Cl, K, Si > S
9	Japan	blue	Si, Cl, K, S > Al, Ti > Mn, Fe, Zn
10	USA	white	Cl, Si, K > S > Ti
11	USA	white	Cl, K > Si > S, Ti > Al > (Fe), (Zn)
12	USA	white	Cl, K, Si > S > (Al)
13	Greece	brown	Si > Cl, K > S > Zn > Cr, Mn, Fe, Al, Ti
14	Turkey	brown	Cl, K > S, Si > Fe, Zn > Ca, Cr, Mn, Al > Cu
15	Turkey	red	Cl, K, Zn > Si, S, Cr > (Fe), (Al)
16	Israel	red	S > Cl, K, Zn > Si, Ca, Cr > (Cu)
17	Korea	white	Si, Cl, K > Mg, S, Ti, Zn
18	Canada	white	Cl, K > Si > S, Ti > (Fe), (Zn)
19	Japan	yellow	Cl, K, S, Si > Mg, Al > (Ti), (Fe), (Cu), (Zn)

^aThe elements are listed in decreasing order of signal intensities. Signals of nearly identical intensity are separated by a comma; > is used to illustrate a considerable difference in signal intensities. The elements in parentheses are found in concentrations close to the detection limit of the method used.

Tracor TN 5500 EDS system). Table 1 shows the elemental composition of the various match heads examined. These compositions are similar to those reported by Andrasko [5] and are consistent with the match head formulation described by Kirk and Othmer [6]. It can be seen that the common denominator for all compositions is the presence of four elements: K, Cl, Si, and S. While K and Cl are always major elements, Si and S may vary in concentration depending on the manufacturer. Figures 1, 2, and 3 are examples of such variation. Potassium and chlorine in a match head originate from KClO_3 , and S is, in most cases, elemental sulfur [5]. Kirk and Othmer [5] mention that lead thiosulfate may serve as a sensitizer; however, we have not detected this compound among the examined match heads nor was it reported by Andrasko [5].

To complement the information obtained by SEM/EDS analysis for the identification of match heads, spot tests were carried out to verify the presence of chlorate ion and elemental sulfur. The spot test for chlorate ion was carried out according to the following procedure [7]: A drop of 5% (w/v) aniline sulfate and a drop of concentrated sulfuric acid were added to a small amount of the sample and the results were observed with a stereomicroscope. The order of addition is important, since addition of sulfuric acid first may ignite the match head. Appearance of a blue color indicates the presence of chlorate. This spot test is specific for chlorate and bromate ions among inorganic oxidizing anions [7]. Bromate may be excluded by SEM/EDS analysis.

To verify the presence of elemental sulfur, an original spot test was developed based on the reduction of sulfur to sulfide ion by hydrazine [8]:



The sulfide ion is identified by a black precipitate formed with a saturated solution of lead acetate. The procedure used is as follows:

A drop of saturated solution of lead acetate was added to a small amount of the sample,

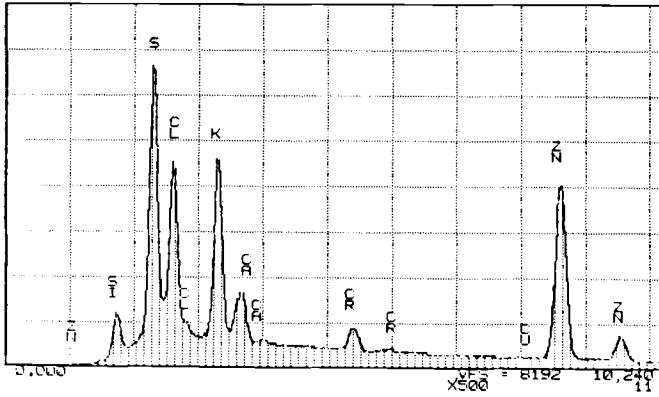


FIG. 1—X-ray spectrum of the Israeli match head (Sample 16 in Table 1).

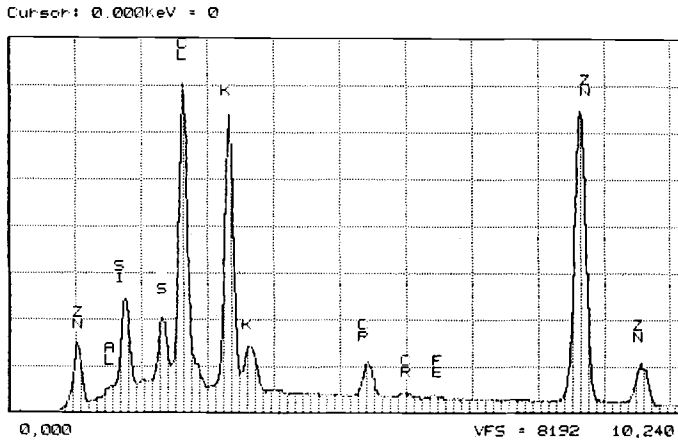


FIG. 2—X-ray spectrum of the Turkish match head (Sample 15 in Table 1).

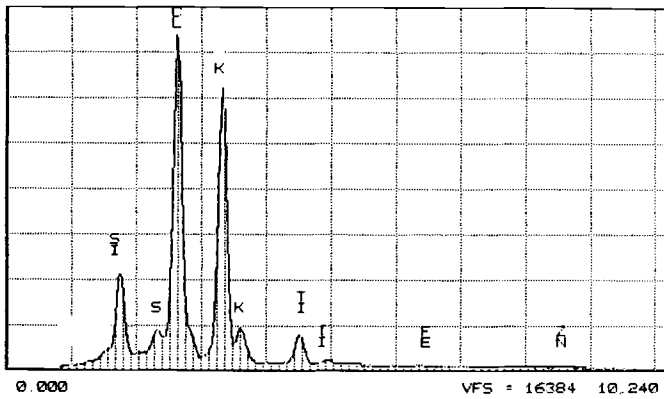


FIG. 3—X-ray spectrum of the Canadian match head (Sample 18 in Table 1).

which was observed with a stereomicroscope, followed by a drop of hydrazine hydrate. The appearance of a black color after about 5 min indicated the presence of elemental sulfur. The above order of addition of the reagents provides a means to ensure that the color formed from elemental sulfur and not sulfide ion. Sulfite and sulfate ions do not produce a black color in the above spot test. Thiosulfate gives a positive result; however, this anion may be expected in match head formulation only in combination with lead [6]. The above spot tests may be performed on the samples prepared for SEM/EDS in cases where a very small quantity of sample is available.

Microspectrophotometry (Docuspec TM/I Nanometrics Inc.) was tried for color characterization of Israeli (red) match heads. However, we found that the variation in the reflectance spectra was too large to be useful as a characteristic feature. The technique was not tried for other colored match heads in this study.

Examination of Post-Explosion Debris

The above procedure for detection and identification of match heads was applied in 13 real cases of explosions of improvised pipe bombs. The pipe fragments collected from the scene were examined with a stereomicroscope for the presence of small fragments similar in color and/or morphology to those of the match heads examined in the study. In 10 cases we found a small amount of minute red fragments (about 0.1 mm in size). Usually the fragments were found in the pipe threads and in the cap (Figs. 4 through 6). These fragments were examined according to the procedure described above for match heads.

The SEM/EDS spectra of the red fragments (Fig. 7) resembled those of Turkish and Israeli match heads in our database (Table 1 and Figs. 1 and 2). The intensity of the sulfur peak in these fragments was, however, much less than that in the Israeli match heads and significantly less than that in Turkish match heads. This observation does not necessarily exclude the fragments as originating from Israeli or Turkish match heads.

To account for the decrease in sulfur peak intensity, the following explanation may be proposed. During the explosion of the improvised device, the match heads that remain intact still may be exposed to high temperatures, which may cause a partial vaporization of sulfur (boiling point, 444.6°C). To verify this hypothesis, the following experiments were performed. Match heads of five brands (Samples 3, 13, 15, 16, and 18 in Table 1)



FIG. 4.—Portion of exploded pipe in which a small red fragment was found.

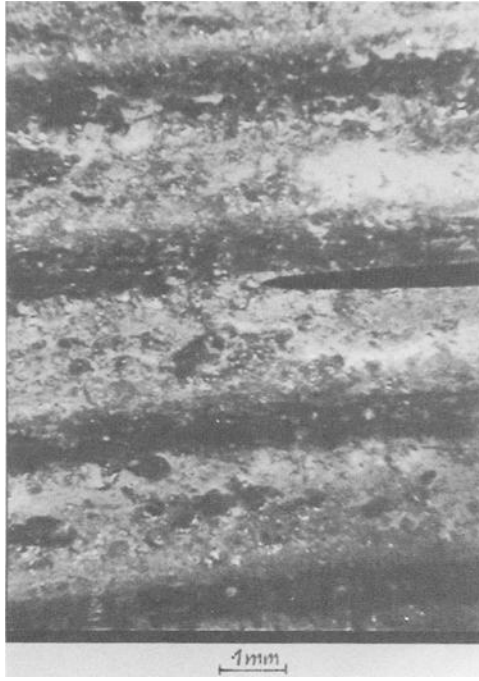


FIG. 5—A red fragment (an arrow points towards the fragment) in the pipe portion shown in Fig. 4.

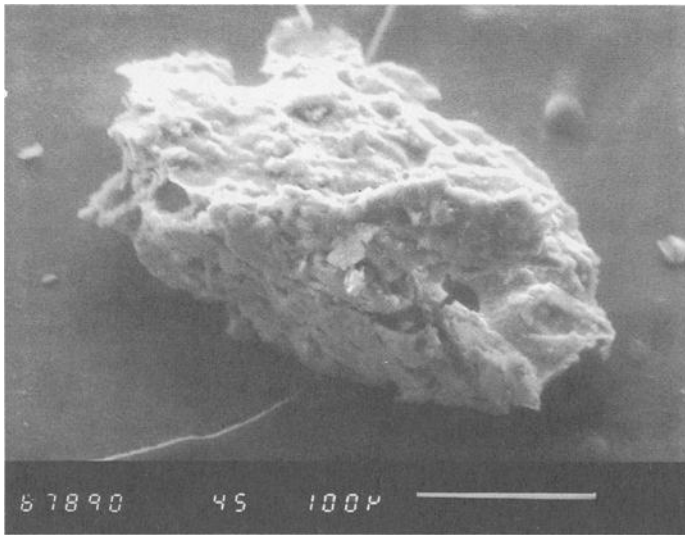


FIG. 6—An SEM micrograph of the red fragment shown in Fig. 5.

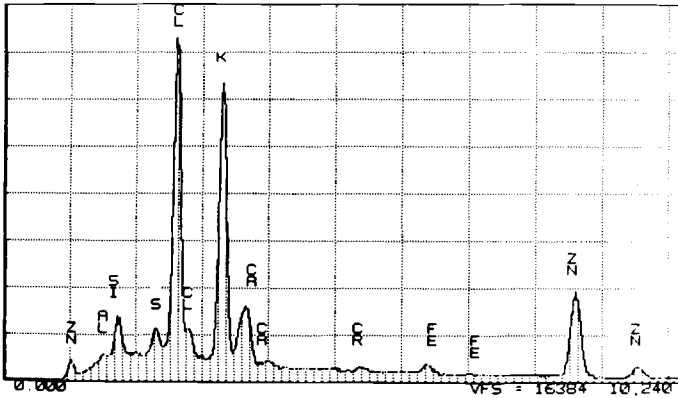


FIG. 7—X-ray spectrum of the red fragment shown in Fig. 5.

were heated in an oven for 1 h at a temperature of 200°C (at temperatures of 250 to 300°C, some of the matches ignited).

In the unheated match heads of Brands 13 and 16, the sulfur peak in the X-ray spectrum was high and that in Brands 3, 15, and 18 was low. Following heating, a considerable decrease in the intensity of the sulfur peak was observed compared with that of the unheated match heads (for example, Figs. 8 and 9). In spite of the decrease, elemental sulfur was detected by the spot test in small scrapings from all the heated match heads. A similar decrease was observed from burnt match heads (for example, Figs. 10 and 11).

To account for the presence of iron in the scrapings from casework, the following explanation may be proposed: The improvised explosive devices with match head scrapings are prepared in galvanized steel pipes with threaded caps. During the explosion, unreacted scrapings impact with the pipe or the cap and this contact results in the presence of iron in the X-ray spectrum of the scrapings. To verify this assumption experimentally, the match heads were rubbed against galvanized steel pipes and examined by SEM/EDX. The spectrum obtained included an iron peak.

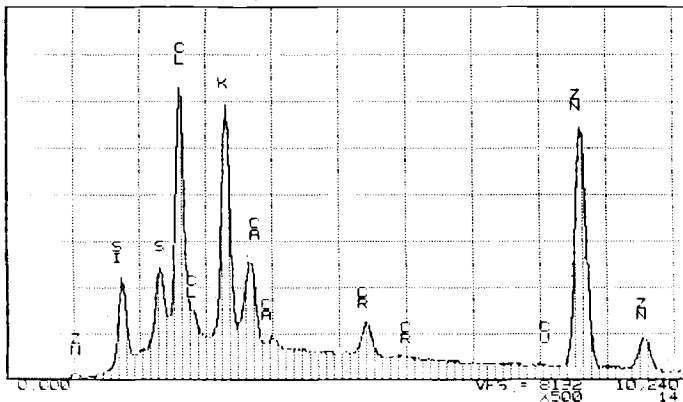


FIG. 8—X-ray spectrum of the Israeli match head (Fig. 1) heated for 1 h at 200°C.

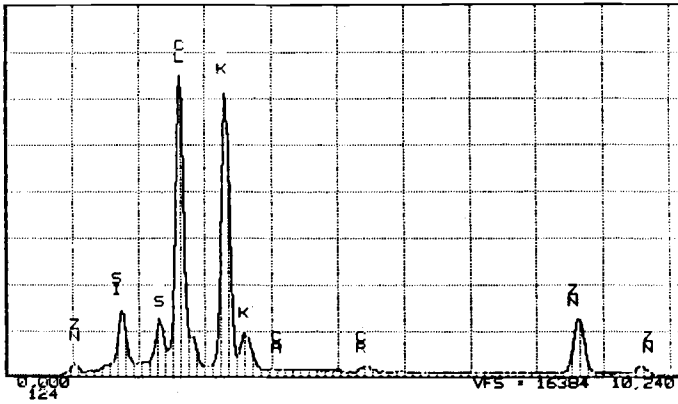


FIG. 9—X-ray spectrum of the Turkish match head (Fig. 2) heated for 1 h at 200°C.

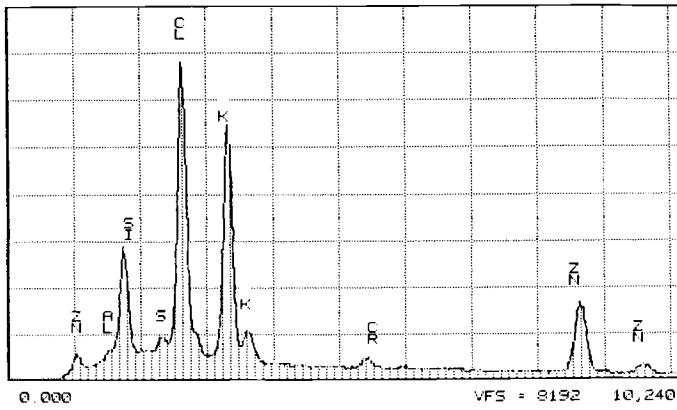


FIG. 10—X-ray spectrum of the Israeli (Fig. 1) burnt match head.

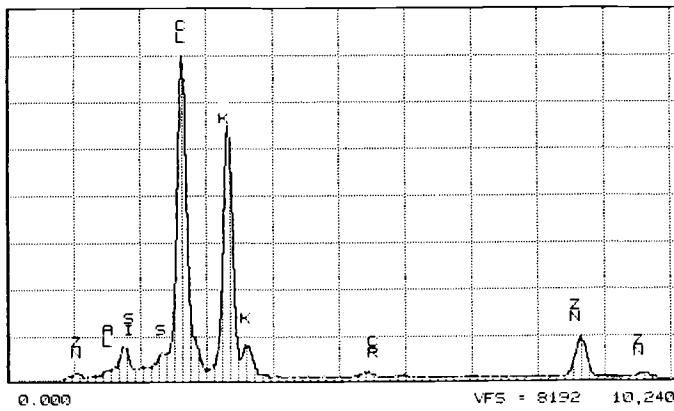


FIG. 11—X-ray spectrum of the Turkish (Fig. 2) burnt match head.

Conclusion

The combination of optical microscopic examination, SEM/EDS, and spot tests for chlorate ion and elemental sulfur may serve as practical proof that the sample originated from match heads, especially if there are match heads for comparison. This type of procedure is much more specific for match head residues than bulk solvent extraction [9,10,11].

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