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The Contribution of Trace Elements from Smokeless Powder to Post Firing Residues

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ABSTRACT: The smokeless powders in 22 kinds of ammunitions seized from one of the Japanese gang groups were analyzed by scanning electron microscopy/energy dispersive X-ray microanalysis (SEM/EDX). Copper(Cu), sulfur(S), potassium(K), silicon(Si), aluminum(Al), calcium(Ca), iron(Fe), chlorine(Cl), and barium(Ba) were detected. Cu was found in all samples. One sample contained a high amount of Ba. One part of the burnt smokeless powder was found to contain Cu, K, Ca, Fe and S, the other part contained Cu, Fe, and zinc(Zn). It has been reported that the elements in gunshot residues originate from a bullet and/or a primer. However, this demonstrates that smokeless powder could be the source of some of the elements detected.

KEYWORDS: forensic science, smokeless powder, scanning electron microscopy, energy dispersive X-ray microanalysis, gunshot residue, copper, inorganic elements

When a firearm is discharged, an assortment of vaporous and particulate materials are expelled in the area around the firearm. Those materials are called gunshot residues(GSRs). GSRs have been detected and identified by many analytical methods such as neutron activation analysis (NAA) (1), flameless atomic absorption spectroscopy (FAAS) (2), inductively coupled plasma/atomic emission spectrometry (ICP/AES) (3,4), auger electron spectroscopy (AES) (5), and scanning electron microscopy/energy dispersive X-ray microanalysis (SEM/EDX) (6–17). SEM/EDX is now a well-established method and applied in many forensic laboratories (17). One of the purposes of SEM/EDX method is the detection of GSRs to identify the shooter or the firing situation. Additionally, this method is useful to characterize the types of cartridges or bullets discharged at the shooting scene. There are many reports about SEM/EDX of GSRs and its anticipated sources. However, there is little reported work analyzing smokeless powders mostly by SEM/EDX. The component of smokeless powder is nitrocellulose, so the elements in the residue after firing are not expected. Therefore, a chromatographic approach (18,19) is commonly applied to identify the residue of smokeless powder instead of SEM/EDX.

Recently, we have had an occasion to seize over 2,000 illegal rounds of ammunition from only one local Japanese gang group. Those were classified into 22 types by the head stamps. We analyzed the smokeless powders in the ammunition by SEM/EDX. We found that it was possible for GSRs to contain elements from burnt smokeless powders.

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Methods

Equipment

The SEM/EDX used was a Hitachi SEM 2100S combined with a Horiba EDX-EMAX 3700.

Smokeless Powders

Twenty-two kinds of ammunition seized from one of the Japanese gang groups are shown in Table 1. Those were manufactured in 6 nations, such as the People's Republic of China (shown as (China) in Table 1), Czechoslovakia, Finland, the Republic of Korea (Korea), the Republic of the Philippines (Philippine), and the United States of America (U.S.A.). The smokeless powder particles were randomly sampled from each cartridge prior to SEM/EDX.

SEM/EDX

With most manufactures, it is likely that a final lot of propellant is blended from several sub-lots in order to achieve the ballistic properties desired by the end user. The number of sub-lots used for a final lot is not constant and the composition of the sub-lots may vary. Therefore, ten smokeless powder particles were sampled randomly from each cartridge and analyzed by SEM/EDX after carbon coating. Those analyses were done by "area mode" at a magnification of 100 and 20 kV.

After analysis by "area mode" for sample-6 (Table 1), one of the particles was examined again by "point mode" for a comparison of the results.

Any one particle of sample-1 was cut in half. The cross section and the surface were analyzed directly by "point mode" to determine the elemental distribution differences between the inner and the outer layer.

The relative peak intensities of elements were normalized as shown in Fig. 1; e.g., a peak height of the top peak = "a," the observed peak height = "b," the relative peak intensity (%) = "b/a $\times$ 100." The results were evaluated using statistics, such as a mean and a standard deviation (SD). A peak was detected by the mean of relative intensity larger than 2%.

Burning Experiment

Many Tokarev-type guns are smuggled into Japan from China and/or Russia. Therefore, we have more opportunities to see the cartridge cases from this type of gun.

TABLE 1—*Samples of 22 kinds of ammunitions seized from the Japanese gang group.*

Sample	Stamp	Caliber	Cartridge	Bullet	Nation
1	‖77	7.8*	Cu plating on brass	Cu plated	China
2	△ 9mm 88 NIC	9.0*	Brass	Brass plated	China
3	301 85	9.0*	Brass	Cu jacketed	China
4	S&B 9mm BrK	9.0*	Brass	Fe-Ni alloy jacketed	Czechoslovakia
5	S&B ȯ 765 Br ȯ	7.9*	Brass	Fe-Ni alloy jacketed	Czechoslovakia
6	LAPUA 32 S&W LONG	7.8†	Brass	Non-jacketed	Finland
7	PMC 38 SPL	9.0†	Ni plated on brass	Non-jacketed	Korea
8	SB 38 SPL	9.0†	Brass	Cu jacketed	Philippine
9	SB 85 45 ACP	11.4*	Brass	Cu jacketed	Philippine
10	SB 87 45 ACP	11.5*	Brass	Cu jacketed	Philippine
11	Federal 38 Special	9.0†	Ni plated on brass	Non-jacketed	U.S.A.
12	FC 32 AUTO	7.9*	Brass	Cu plated	U.S.A.
13	R-P 25 AUTO	6.4*	Brass	Cu jacketed	U.S.A.
14	R-P 32 AUTO	7.9*	Brass	Cu jacketed	U.S.A.
15	R-P 357 MAGNUM	9.0†	Ni plated on brass	Non-jacketed	U.S.A.
16	R-P 380 AUTO	9.0*	Brass	Cu jacketed	U.S.A.
17	SUPER-X 357 MAGNUM	9.0†	Brass	Cu jacketed	U.S.A.
18	W-W 32 AUTO	7.9*	Brass	Cu jacketed	U.S.A.
19	W-W 32 S&W LONG	7.7†	Brass	Non-jacketed	U.S.A.
20	W-W SUPER 357 MAGNUM	9.0†	Brass	Non-jacketed	U.S.A.
21	WCC 82	11.5*	Brass	Cu jacketed	U.S.A.
22	WINCHESTER 357 MUG	9.1†	Ni plated on brass	Cu jacketed	U.S.A.

*Revolver.
†Automatic.

The burning experiment was done for sample-1. Five particles were ignited on a clean glass disk. The residue(S-1) was collected on a carbon sticky tab of an aluminum SEM stub. The SEM stub was searched manually using the back scattered electron imaging mode. The particles of interest on the stub were analyzed subsequently by EDX.

The elements detected by SEM/EDX were aluminum(Al), silicon(Si), sulfur(S), chlorine(Cl), potassium(K), calcium(Ca), barium(Ba), iron(Fe), and copper(Cu) as shown in Table 2. The values in the table were evaluated by "mean ± SD." In contrast with other samples, sample-1, -5, and -6 contained relatively high amounts of Al.

The comparison of analytical result by "area mode" and "point mode" for sample-6 is shown in Fig. 2.

One particle of sample-1 (Table 2) was cut in half and the point analysis was done with its cross section and the surface. The elements detected on the surface were the same as for the cross section (Fig. 3).

The SD of Cl of the cross section was very large and the minimum intensity was almost 0%.

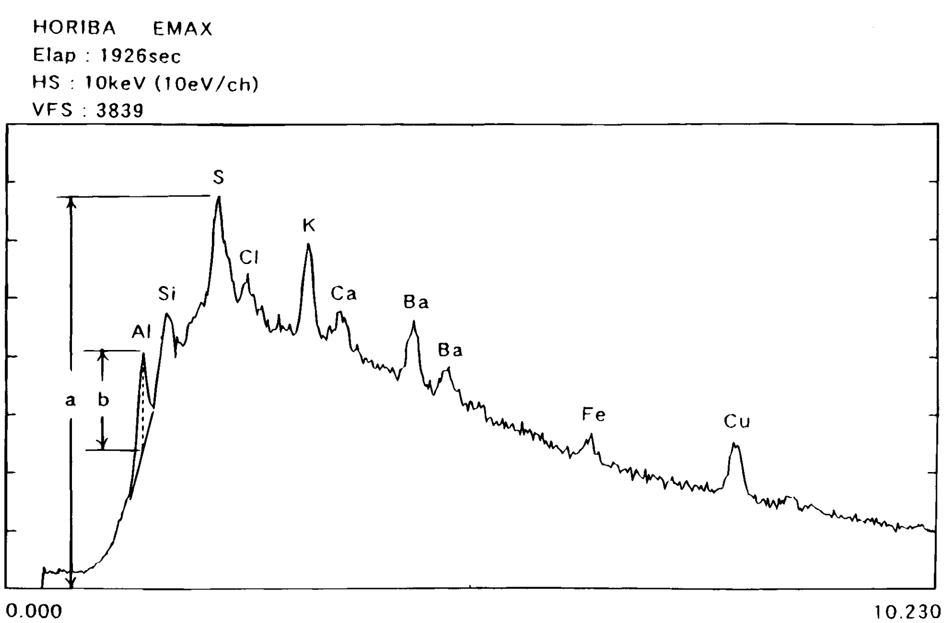

FIG. 1—*The normalization of peak intensity (%). The EDX spectrum is obtained from sample-6. A peak height of the top peak (S in figure) = a, the observed peak height (Al) = b, the relative peak intensity (%) = b/a × 100. Peaks were detected over 2%.*

TABLE 2—*The SEM/EDX results of smokeless powders.*

Element Sample	Al	Si	S	Cl	K	Ca	Ba	Fe	Cu
1	10.2 ± 9.3	6.3 ± 6.1	14.1 ± 4.6	7.9 ± 1.5	22.9 ± 6.8	24.1 ± 8.7	ND	5.9 ± 3.8	8.3 ± 6.4
2	2.1 ± 2.8	10.9 ± 3.2	ND	ND	ND	ND	ND	ND	9.6 ± 1.4
3	4.5 ± 6.2	10.7 ± 6.0	ND	3.1 ± 5.0	ND	ND	ND	ND	10.7 ± 1.7
4	ND	ND	5.1 ± 2.7	3.9 ± 0.7	ND	ND	ND	ND	4.5 ± 2.6
5	13.9 ± 5.8	ND	ND	3.3 ± 1.0	2.5 ± 1.7	ND	ND	20.6 ± 11.2	3.6 ± 0.9
6	10.0 ± 1.5	9.7 ± 1.6	20.7 ± 1.8	5.9 ± 0.5	22.4 ± 2.4	7.3 ± 3.4	12.2 ± 7.6	5.9 ± 3.3	12.8 ± 5.6
7	ND	ND	12.9 ± 5.6	ND	ND	3.2 ± 2.7	ND	ND	14.0 ± 8.1
8	ND	ND	ND	ND	2.6 ± 1.8	ND	ND	ND	3.5 ± 1.4
9	ND	3.4 ± 2.2	5.9 ± 2.0	ND	11.3 ± 6.0	ND	ND	ND	3.5 ± 2.6
10	ND	ND	29.3 ± 17.4	ND	24.5 ± 8.8	ND	ND	ND	3.9 ± 1.6
11	ND	8.1 ± 4.6	2.8 ± 4.5	7.4 ± 1.3	6.2 ± 3.9	ND	2.4 ± 2.2	17.3 ± 6.4	4.8 ± 1.4
12	3.5 ± 1.8	4.7 ± 2.9	2.1 ± 2.6	ND	ND	ND	ND	15.2 ± 9.1	3.4 ± 2.5
13	ND	17.7 ± 9.7	16.1 ± 8.0	ND	25.1 ± 9.9	5.5 ± 4.9	ND	ND	4.1 ± 1.8
14	ND	ND	11.3 ± 4.9	ND	ND	ND	3.9 ± 2.5	ND	4.4 ± 1.9
15	ND	ND	10.5 ± 7.8	ND	ND	ND	ND	ND	3.8 ± 2.2
16	ND	ND	7.3 ± 3.6	ND	11.7 ± 6.9	ND	ND	ND	3.9 ± 2.0
17	ND	2.4 ± 1.5	2.1 ± 1.2	ND	ND	ND	ND	ND	3.5 ± 1.6
18	ND	2.1 ± 1.6	26.1 ± 9.1	ND	ND	ND	ND	4.4 ± 5.7	3.6 ± 4.1
19	ND	6.6 ± 3.2	24.7 ± 12.0	ND	17.6 ± 4.6	ND	ND	ND	3.2 ± 2.2
20	ND	ND	22.8 ± 18.2	ND	ND	ND	ND	ND	3.7 ± 1.8
21	ND	ND	5.9 ± 3.4	ND	18.4 ± 5.9	ND	ND	ND	3.7 ± 3.8
22	ND	5.2 ± 2.9	15.7 ± 8.9	ND	29.1 ± 5.3	ND	ND	ND	4.5 ± 2.8

Results are shown by the "mean of the relative intensity (%) ± SD". ND = not detected.

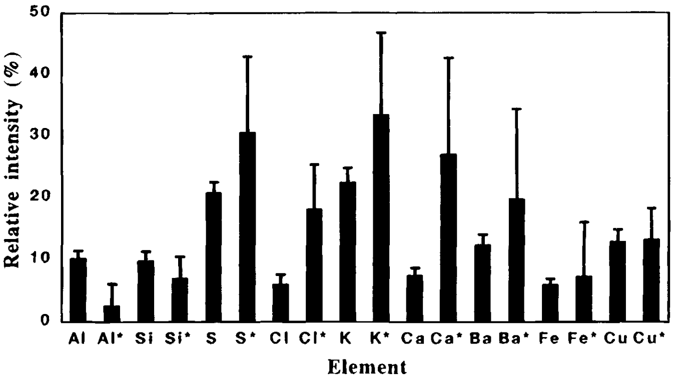

FIG. 2—*The comparison of two analytical modes, "area mode" (non-asterisk on the element name) and "point mode" (asterisk on the element name), for sample-6. The solid columns are the mean. SD bars are also shown.*

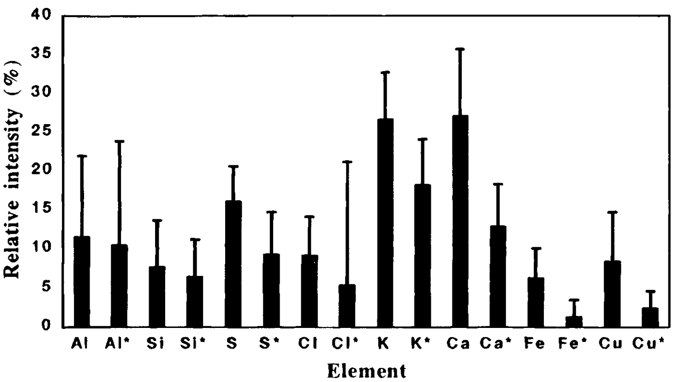

FIG. 3—*The comparison of elemental distribution of sample-1 between the surface (non-asterisk on the element name) and the cross section (asterisk on the element name).*

The SEM/EDX of the edge of sample-1 resulted almost Al (Fig. 4). All samples analyzed in this study contained Cu as shown in Table 2 and Fig. 5. Sample-1, -2, -3, -6, and -7 have rather high levels of Cu compared with other samples.

Figure 6 shows a SEM image of S-1 (see in the text, *burning experiment*). A porous surface was observed in contrast to typical spherical GSRs. The part of S-1 was found to consist of Si, S, K, Ca, Fe, and Cu (Fig. 7). Figure 8 shows EDX spectrum of the one part of S-1 which consisted of Cu and by small amounts of zinc(Zn), and Fe.

Discussion

We examined many kinds of ammunitions seized from one local Japanese gang group; called "Yakuza or Boryoku-dan." Those cartridge cases totaled about 2,000. The ammunitions were classified by the head stamps before the identification of a propellant ability.

Sample-6 (Table 2) has nine kinds of elements. The comparison of those average elemental composition on the ten particles and on the one of its surface is shown in Fig. 2. The SD of every elemental peak intensities on the surface analyzed by "point mode" were larger than that of the ten particles by "area mode." This result suggests that the presumptive sources of those elements are dispersed on the surface. On the other hand, the means of S, Cl, K, Ca, and Ba in the point analysis are higher than the average mean of ten particles. A single, double and/or triple-based smokeless powder is generally prepared to be flameless by the addition of potassium sulfate, sodium sulfate, potassium nitrate, barium nitrate, and other alkaline salts (18, 20). The result of elements detected on sample-6 suggests that some those chemicals are present in the smokeless powders. But, these approach will not allow the determination of the source of the elements.

Sample-1, -2, -3, -5, -6, and -12 contained Al as shown in Table 2. The SEM/EDX of the edge of sample-1 resulted almost Al as mentioned before (Fig. 4). S-1, the burnt residue of sample-1, was lack of Al because of its relatively easy vaporization (Fig. 8). Cryolite (Al compound) is sometimes added to a triple-based smokeless powder (19). Two possible sources were assumed, the additives of Al compound and the dust of an Al-made priming cup. Anyway, burning experiment of sample-1 confirmed that the Al in GSRs was likely from the primer and not the smokeless powder.

Cu is an important element to distinguish whether the bullet jacketed or not. The solution of this problem would be easy when we could find metallic particles consisting only of Cu, Pb, Ni, Zn, or other simple combination of those elements. Usually, Cu-containing chemicals are not utilized in a smokeless powder. Therefore, the Cu in the smokeless powders were doubted a contamination from the construction process of ammunitions. But, non-jacketed sample-6 and -7 have a relative high amount of Cu. Sample-2 (brass plating bullet) has a similar level of Cu contrast to Cu-jacketed sample-1 and -2, Table 2, Fig. 5. Beside, the core of sample-1 has Cu even it is a low level (Fig. 3). There is no definitive correlation between the Cu in the smokeless powders and the composition of bullets. The origin of a high amount of Cu on the surface was likely from the dust of brass cartridge by the relative large SD. The proper origin of Cu in the core was the equipments used in the production process of nitrocellulose. It is usually made from an alloy of Cu to meet safety handling (20).

Mogami et al. (7) reported that the combination of elements in GSRs were rich in variety such as Pb only, Pb-antimony(Sb)-Ba, Pb-Sb-Ba-Si, Pb-Sb-Ba-Cu-Zn, Pb-Sb-Ba-Al-K, Pb-Ba-Si-Ca-Fe-Cu-Zn, and so on. They estimated that those elements were originated from the barrel, bullet, cartridge case, and/or primer.

Harris (10) and Zeichner et al. (13) examined GSRs from the ammunitions having a mercury fulminate based primer. The elements in GSRs analyzed by SEM/EDX were tin(Sn), Sb, mercury(Hg), Si, S, Cu, K, Cl, Al, and so on. They determined that the sources of those elements were the primer mixture, and priming cup.

It has been reported that Cu in GSRs is originated mainly from Cu and/or Cu alloy jacketed bullet, some cases from priming cup. However, the analytical result of burning experiment of sample-1 emphasize that Cu in GSRs is originated partly from smokeless powders. Those fact may tend to make a misjudgment for the prediction of suspected jacket type.

Sample-6, -11, and -14 contained Ba. Sample-6 was relatively high Ba as shown in Table 2. Therefore, it is also suggested that a part of Ba in GSR is originated from the smokeless powders.

The results in this study indicate that the sources of GSR elements, such as Si, S, Cl, K, Ca, Ba, Fe, Cu, and Zn, are partly from smokeless powders.

The discrimination of the samples each other only by the SEM/EDX analysis was attempted. Using the comparison of the mean of elemental level could classify them. However, the elemen-

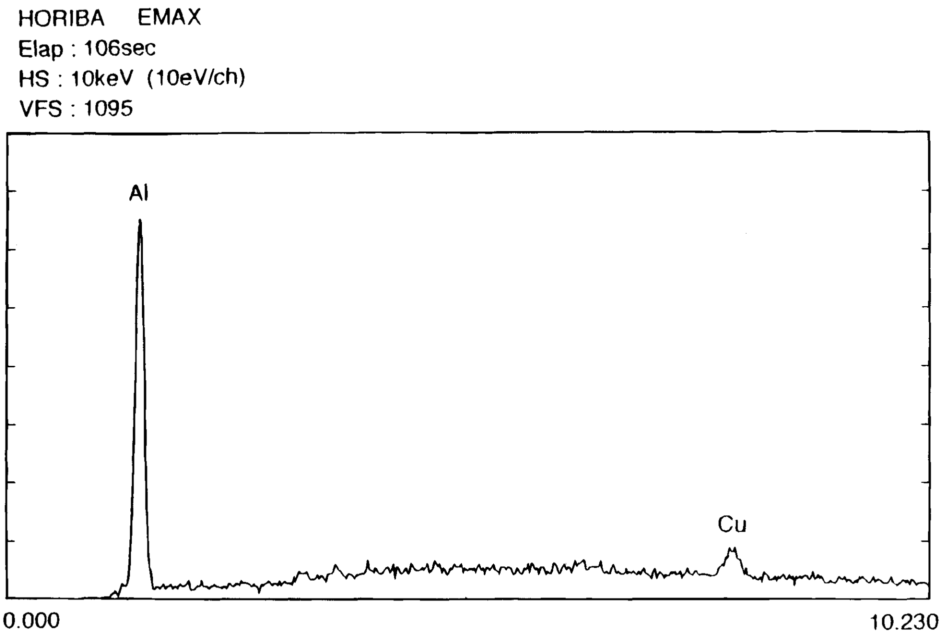

FIG. 4—*EDX spectrum of the edge of smokeless powder sampled from sample-1, containing a high amount of Al.*

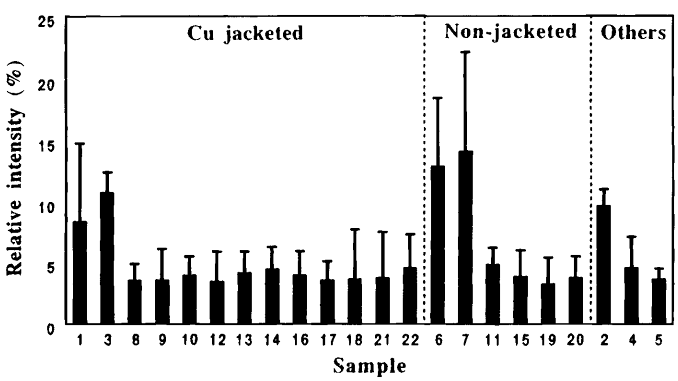

FIG. 5—*The comparison of Cu on the samples. Samples are lined by the bullet type.*

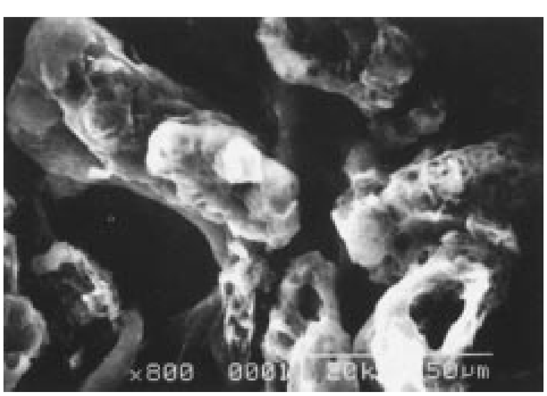

FIG. 6—*SEM image of the burnt residue of sample-1 (S-1).*

tal level varied wide. Further more, it is usually hard to find out the enough smokeless powder particles from an actual firing scene. After all, it seemed to be difficult to discriminate each other only by SEM/EDX for a few particles.

Conclusion

We examined 22 kinds of smokeless powders by using SEM/EDX and Cu, S, K, Si, Al, Ca, Fe, Cl, Ba were detected. An approach of the discrimination each other only by SEM/EDX was difficult by means of their large SD.

It is supposed that the sources of Cu, S, K, Si, Al, Ca, Fe, Cl, Ba, Zn in GSRs are not only from bullet, cartridge case, and/or primer, but from smokeless powders.

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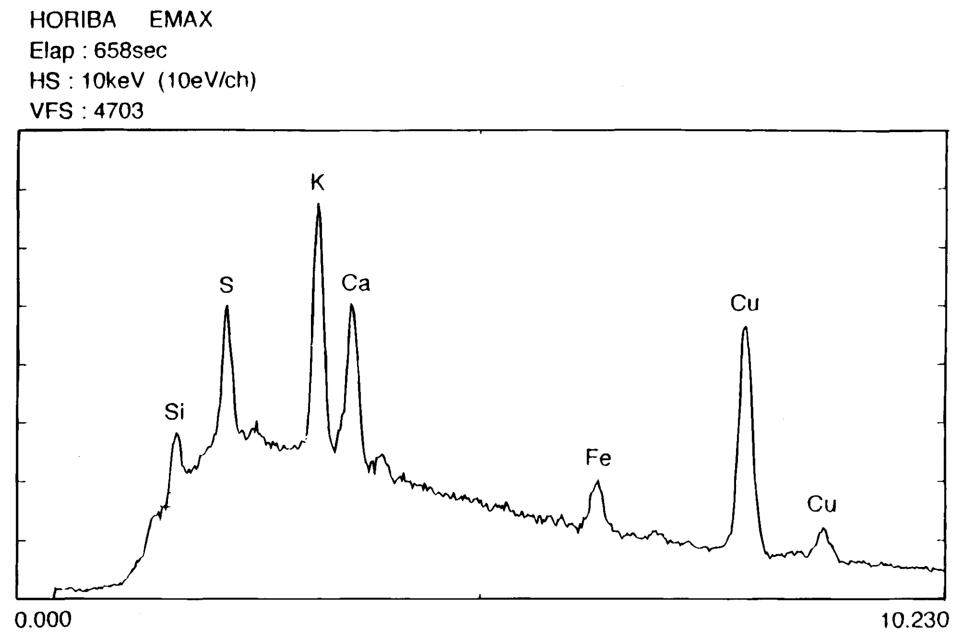

FIG. 7—*Typical EDX spectrum of S-1.*

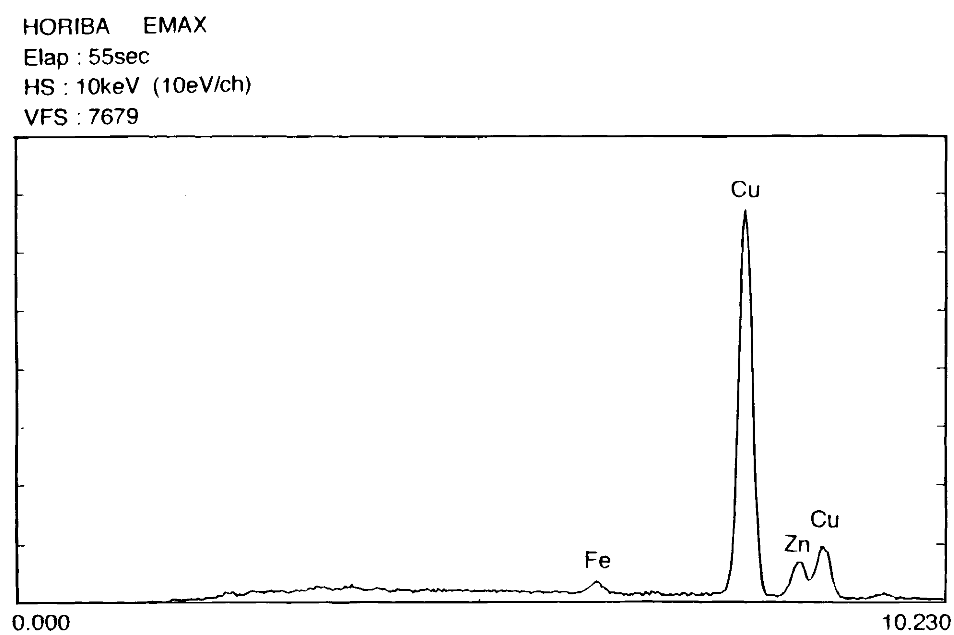

FIG. 8—*EDX spectrum of S-1, containing a high amount of Cu, accompanied by small amounts of Zn, and Fe.*

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