

TECHNICAL NOTE

Masaaki Kasamatsu,¹ M.Sc.; Yasuhiro Suzuki,¹ Ph.D.; Ritsuko Sugita,¹ M.Sc.; and Shinichi Suzuki,¹ Ph.D.

Forensic Discrimination of Match Heads by Elemental Analysis with Inductively Coupled Plasma-Atomic Emission Spectrometry

ABSTRACT: In arson and bombing cases, matches are often used as the ignition method. We have investigated the use of elemental analysis by inductively coupled plasma-atomic emission spectrometry to discriminate match heads used in arson cases. Six elements, magnesium, aluminum, calcium, iron, zinc, and barium, in match heads were detected after the match heads were dissolved in HNO₃, and these elements were quantified in 8 wood stick matches and 5 paper stick matches by means of calibration curves prepared from standard sample solutions. Using this method, we were able to distinguish all the matches from one another both before and after combustion. The method has the potential to be very useful for resolving arson cases.

KEYWORDS: forensic science, discrimination, match head, combustion, elemental analysis, inductively coupled plasma-atomic emission spectrometry, X-ray diffraction analysis

Matches are important items of physical evidence in arson and bombing cases. If a match retrieved from a crime scene showed elemental similarity to matches confiscated from a suspect, the similarity could provide corroborative evidence connecting the suspect with the scene. Forensic discrimination of matches has been carried out by the observation of morphological characteristics, such as the shape of the matchstick and the color of the match head (1). Combining these conventional comparisons with multi-elemental analysis can provide additional information for the discrimination of match heads.

In the forensic discrimination of trace physical evidence by means of elemental analysis, it is important to measure as many elements as possible over a wide concentration range because high similarity among many elements detected can increase the evidential value of the samples examined. For this purpose, the capability for simultaneous multi element analysis is preferable because it allows measurement of a number of elements in a short time.

Application of scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDX), X-ray fluorescence (XRF), and atomic absorption spectrometry (AAS) has been studied for the examination of matches as physical evidence (1–3). However, owing to their poor sensitivity, SEM/EDX and XRF are not suitable for trace element analysis. AAS would be a complex and time-consuming method to measure many elements, because it is a technique for single-element analysis.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is a powerful analytical tool for simultaneous multi-elemental analysis. The technique has a wide dynamic range and high sensi-

tivity for trace elements (4,5). These advantages make ICP-AES an ideal tool for the elemental analysis of forensic samples (6–9).

In this study, ICP-AES was applied to match heads for the discrimination of match samples by comparison of their elemental compositions. The effect of combustion on the analytical results was also investigated.

Materials and Methods

Apparatus

The operating conditions for the ICP-AES instrument used in this study (SPS-1700HVR, Seiko Instruments Inc., Chiba, Japan) are shown in Table 1.

The operating conditions for X-ray diffraction analysis (RINT 2500, Rigaku Corp., Tokyo, Japan) were as follows: target, Cu; acceleration voltage, 40 kV; current, 40 mA; scan speed, 4 deg/min.

Reagents

The nitric acid used for this experiment was an ultrapure grade for measuring poisonous metals (Kanto Chemical Co. Inc., Tokyo, Japan). Multi-elemental working standard solutions containing 1 µg/mL or 10 µg/mL of each element in 5% nitric acid by volume were prepared for calibration by mixing single-element standard solutions for atomic absorption spectrometry (Kanto Chemical Co. Inc., Tokyo, Japan). Purified water was prepared with a Milli-Q system (Nihon Millipore Kogyo Ltd., Osaka, Japan) and used throughout the experiments.

Samples

Thirteen matches were collected and analyzed in order to determine the discrimination capability by comparison of minor and/or

¹National Research Institute of Police Science, 6-3-1 Kashiwanoha, Kashiwa, Chiba 277-0882, Japan.

Received 18 Sept. 2004; and in revised form 9 March 2005; accepted 12 March 2005; published 25 May 2005.

TABLE 1—Operating conditions for ICP-AES.

Plasma Conditions	
RF frequency	27.12 MHz
RF power	1.3 kW
Plasma gas flow rate	16 L/min
Auxiliary gas flow rate	0.4 L/min
Carrier gas flow rate	0.4 L/min
Observation height	10 mm above work coil
Nebulizer	
Sample uptake rate	0.5 mL/min
Wavelength	
Mg 279.8 nm	Al 396.2 nm
Ca 422.7 nm	Fe 238.2 nm
Zn 202.5 nm	Ba 230.4 nm
Data acquisition	
Detection	Sequential
Integration time	1 sec
Repetitions	3 times

TABLE 2—Match samples analyzed.

No.	Procurement	Package	Material of Matchstick	Color of Match Head
B1	Purchase	Box	Wood	Red
B2	Purchase	Box	Wood	Brown
B3	Purchase	Box	Wood	Red
B4	Free distribution	Box	Wood	White
B5	Purchase	Box	Wood	Red
B6	Purchase	Box	Wood	Red
B7	Free distribution	Box	Wood	White
B8	Purchase	Box	Wood	Brown
P1	Free distribution	Book	Paper	White
P2	Free distribution	Book	Paper	White
P3	Free distribution	Book	Paper	White
P4	Free distribution	Book	Paper	White
P5	Free distribution	Book	Paper	White

trace element concentrations. Six of the samples were commercially available matches, and the others were advertising matches. The procurement methods and colors of the match heads are shown in Table 2.

Procedure

Sample solutions for ICP-AES were prepared as follows. A match head was scraped from the wood or paper base with a blade. About 10 mg of the match head was accurately weighed on a microbalance (accuracy limit, 100 µg) and then placed in a microcentrifuge tube. After the addition of 1 mL of concentrated HNO₃, the tube was capped and left overnight. The sample was centrifuged at 5000 rpm for 5 min, and the supernatant was separated. 1 mL of 5% HNO₃ was added to the precipitate and again centrifuged, with the supernatant added to the first. This was repeated one additional time. The supernatants were collected in a volumetric flask and then diluted to 20 mL with purified water. Six elements (Mg, Al, Ca, Fe, Zn, and Ba) in each sample solution were determined by ICP-AES.

Some of the precipitates collected in the pretreatment process were also analyzed by XRD. The precipitates were dried and dispersed on a quartz sample holder with collodion.

Results and Discussion

Selection of Elements for Discrimination

Before quantitative analysis, we qualitatively analyzed the elemental compositions of sample solutions by scanning the profiles of all the measurable elements using ICP-AES. Six minor and/or trace elements (Mg, Al, Ca, Fe, Zn, and Ba) were deemed to be effective for discrimination because they were detected in more than half of the samples and because the emission intensities of these elements showed large variations among the different samples. Although Mitsui et al. reported that Cr and Pb also could be effective for discrimination (2), we excluded these two elements from quantitative analysis because their concentrations were under determination limit in this study.

Analytical Results for Match Samples

We applied the proposed ICP-AES method to 13 kinds of match samples of different origin. The analytical results are shown in Table 3 with the lower limit of determination for each element.

The lower limit of determination corresponds to the lowest concentration in the match head samples calculated from the lower limit of determination of the analytical standard solution. The lower limit

TABLE 3—ICP-AES results for uncombusted match samples.

Sample	Concentration (µg/g*)					
	Mg	Al	Ca	Fe	Zn	Ba
B1	432 ± 11	240 ± 51	2650 ± 160	112 ± 7	—	1020 ± 50
B2	2610 ± 40	240 ± 12	795 ± 29	416 ± 34	8 ± 1	—
B3	265 ± 10	— [‡]	3220 ± 70	94 ± 4	5240 ± 120	1550 ± 320
B4	104 ± 7	—	818 ± 26	70 ± 4	7 ± 1	—
B5	509 ± 17	164 ± 13	4300 ± 130	268 ± 56	—	1940 ± 100
B6	198 ± 24	140 ± 54	835 ± 61	304 ± 125	3290 ± 180	949 ± 41
B7	509 ± 9	280 ± 13	1680 ± 110	205 ± 42	6 ± 1	—
B8	222 ± 18	—	7350 ± 310	711 ± 96	—	17 ± 3
P1	428 ± 5	177 ± 21	1480 ± 30	220 ± 29	—	—
P2	—	—	4320 ± 10	83 ± 4	—	142 ± 2
P3	206 ± 9	333 ± 9	10700 ± 200	210 ± 49	97 ± 4	—
P4	283 ± 1	130 ± 6	1760 ± 60	101 ± 22	8280 ± 60	—
P5	132 ± 2	—	409 ± 15	263 ± 73	1250 ± 10	29 ± 1
LLD [†]	74	116	81	10	3	10

* Mean ± SD (n = 5 for B1–B8, n = 3 for P1–P5).

[†] Lower limit of determination.

[‡] Under determination limit.

TABLE 4—ICP-AES results for combusted match samples.

Sample	Concentration ($\mu\text{g/g}^*$)					
	Mg	Al	Ca	Fe	Zn	Ba
B1	8880 \pm 650	4840 \pm 300	3560 \pm 120	428 \pm 19	— [†]	1220 \pm 100
B2	3650 \pm 360	1300 \pm 120	1160 \pm 506	15100 \pm 2600	18 \pm 3	—
B3	8290 \pm 270	4050 \pm 110	5570 \pm 90	446 \pm 18	7890 \pm 250	2140 \pm 160
B4	908 \pm 36	338 \pm 33	1070 \pm 70	99 \pm 7	12 \pm 6	—
B5	13200 \pm 300	6230 \pm 220	6510 \pm 350	726 \pm 113	10 \pm 9	2640 \pm 280
B6	2930 \pm 150	2160 \pm 80	1470 \pm 60	470 \pm 70	3800 \pm 100	966 \pm 41
B7	11400 \pm 300	5460 \pm 140	2330 \pm 100	507 \pm 81	9 \pm 2	—
B8	1090 \pm 50	391 \pm 19	8300 \pm 172	7240 \pm 800	5 \pm 1	26 \pm 2
P1	5190 \pm 240	2800 \pm 300	2810 \pm 1100	485 \pm 84	6 \pm 5	12 \pm 0
P2	107 \pm 16	394 \pm 97	5370 \pm 220	149 \pm 94	10 \pm 2	247 \pm 2
P3	797 \pm 31	1120 \pm 90	11300 \pm 300	383 \pm 80	93 \pm 2	—
P4	6280 \pm 180	3600 \pm 470	3280 \pm 300	235 \pm 19	11500 \pm 700	—
P5	2570 \pm 130	2140 \pm 70	1440 \pm 230	463 \pm 71	964 \pm 36	58 \pm 2

* Mean \pm SD (n = 5 for B1–B8, n = 3 for P1–P5).

[†] Under determination limit.

of detection was determined from the signal-to-noise ratio. Usually, a 3σ noise value was adopted in these experiments, and the lower limit of determination was denoted by the concentration equivalent to the peak intensity of a 10σ signal-to-noise ratio.

The variation in the analytical values for each element within the samples was sufficiently small compared to the variation between the samples. This result indicates that comparison of the elemental compositions obtained by the proposed method is effective for the discrimination of match samples. It should be noted that intra-sample variations for match samples were slightly larger than the intra-sample variations for other evidential materials, such as glass (10,11), solder (12), and arsenous acid (13). This larger variation might be ascribed to the poor homogeneity of match heads compared with other samples.

Discrimination by Analytical Results

Match samples were discriminated by comparison of the qualitative and quantitative results from analysis of the match heads. Because wood and paper matches can easily be distinguished by the morphology of the matchsticks, the two types of matches were not compared; comparison of the elemental components of match heads is required only for discrimination of match samples within a category.

If the range of average values $\pm 2\sigma$ for two samples did not overlap, they were considered to originate from different sources. If the ranges did overlap, the samples could not be discriminated by the element. The case of Mg, 24 of the 28 pairs of wood matches could be discriminated, and 4 could not. All of the 10 pairs of paper matches could be discriminated.

When all 6 elements were used, the results for each element were compared as described above. If the ranges for one or more elements did not overlap, the match samples were considered to be from different origin. When 6 elements were used, all 28 pairs of matches could be clearly discriminated. This result indicates that multi-elemental analysis results in improved discriminating capability relative to single-element analysis.

Analysis and Discrimination of Burned Match Samples

Match samples recovered at crime scenes are always combusted, whereas control matches seized from suspects are usually uncom-

busted. If the two kinds of samples are to be compared, the effect of combustion on the results obtained from multi-elemental analysis must be investigated. Therefore, we also analyzed match heads taken from combusted samples by the same procedure. The results of multi-elemental analysis for the combusted samples are shown in Table 4.

Four elements, Mg, Al, Ca, and Fe, were detected in all the samples. Zn was found in all but one sample, and Ba was detected in 8 samples. The concentrations of Ca, Fe, Zn, and Ba found in combusted matches were higher than those in unburned ones. This result can be explained in terms of the reduction in the weight of the match heads through combustion. However, concentration increases for Mg and Al were much greater than those for the other 4 elements.

The concentration range of each of the elements in the various samples was significantly larger than the deviation within each sample. However, comparison of the analytical values for 6 elements was also effective for the discrimination of combusted match samples. Discrimination of combusted match samples was also performed as described above. All of pairs could be clearly discriminated using 6 elements. Multi-elemental comparison was also effective for achieving high discrimination among combusted matches.

XRD Spectra of Match Head Residues

X-ray diffraction analysis was used to investigate differences in the crystal structures of burned and unburned match heads. Three samples were prepared by burning sample B1 (Table 2) for 1 sec, 2 sec, and until burned out. These three burned samples and unburned ones were pretreated as described above, and the residues were used for the XRD measurement. The XRD spectra obtained are shown in Fig. 1.

Major peaks, which were considered to be hydrous phyllosilicates, decreased significantly after combustion.

One of the most important results obtained from the XRD experiments was that the peak intensities did not depend on the burning time. This indicates that the destruction of crystals was completed within 1 sec of ignition and was unaffected by additional burning time.

These results indicate that multi-elemental comparison is effective for discrimination of burned match samples, because match heads from a single source should exhibit similar elemental compositions even after combustion.

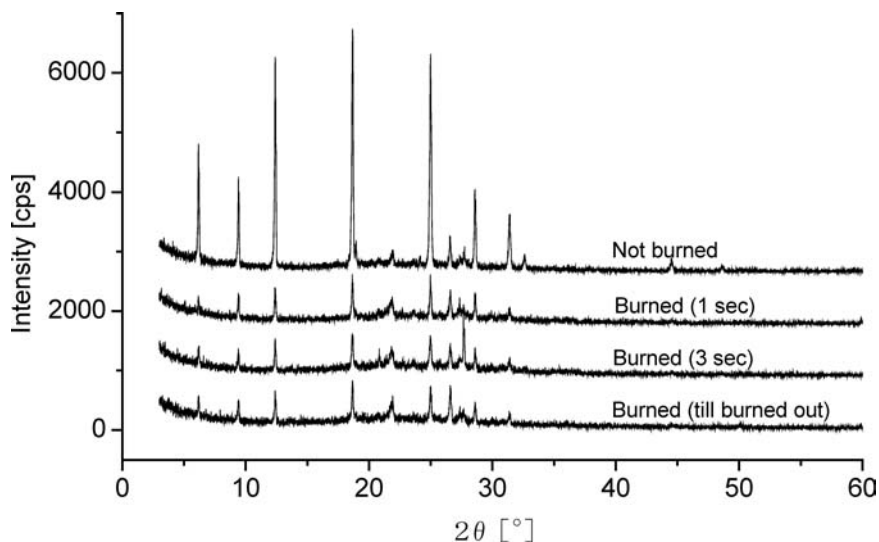


FIG. 1—XRD spectra of match head residue. Sample, B1.

Conclusion

Comparison of analytical results obtained with the method permitted the discrimination of all 28 pairs of 8 wood matches and 10 pairs of 5 paper matches. Multi-elemental comparison was very effective in reducing the number of indistinguishable pairs.

Six elements were used to discriminate between the matches tested. In cases where the average values were sufficiently different, it was found to be an effective discriminator among the matches tested. This technique was also effective for combusted match samples. All pairs were successfully discriminated even after the combustion.

To effectively use this technique in casework, it is recommended that matches be burned before testing to make same condition. The comparison of matches with same condition will be successfully performed.

References

1. Andrasko J. Identification of burnt matches by scanning electron microscopy. *J Forensic Sci* 1978;23(4):637–42.
2. Mitsui T, Miyachi Y. Identification of match head. *REPORTS of the National Research Institute of Police Science, Japan* 1972 Feb;25(1):41–6.
3. Glattstein B, Landau E, Zeichner A. Identification of match head residues in post-explosion debris. *J Forensic Sci* 1991;36(5):1360–7.
4. Shindoh K, Yasui A. Determination of mineral contents in a single grain of rice by ICP-AES. *BUNSEKI KAGAKU* 1997;46(10):813–818.
5. Minakawa M, Uematsu M. Rapid determination of multi-elements in geochemical samples by microwave acid digestion ICP-AES. *BUNSEKI KAGAKU* 2001;50(4):273–9.
6. Kasamatsu M, Suzuki Y, Suzuki S. Determination of toxic metal ions in beverages by inductively coupled plasma atomic emission spectrometry. *Jpn J Sci Tech Iden* 2002;7(1):37–43.
7. Koons RD, Havekost DG, Peters CA. Determination of barium in gunshot residue collection swabs using inductively coupled plasma-atomic emission spectrometry. *J Forensic Sci* 1988;33(1):35–41.
8. Koons RD, Peters CA, Merrill RA. Forensic comparison of household aluminum foils using elemental composition by inductively coupled plasma-atomic emission spectrometry. *J Forensic Sci* 1993;38(2):302–15.
9. Koons RD, Grant DM. Compositional variation in bullet lead manufacture. *J Forensic Sci* 2002;47(5):950–958. [\[PubMed\]](#)
10. Suzuki Y, Sugita R, Suzuki S, Marumo Y. Determination of trace impurities in windshield glass by ICP-MS. *BUNSEKI KAGAKU* 1997;46(10):825–30.
11. Suzuki Y, Kasamatsu M, Sugita R, Ohta H, Suzuki S, Marumo Y. [Forensic discrimination of headlight glass by analysis of trace impurities with synchrotron radiation X-ray fluorescence spectrometry and ICP-MS.](#) *BUNSEKI KAGAKU* 2003;52(6):469–74.
12. Suzuki Y, Kasamatsu M, Suzuki S, Marumo Y. [Forensic discrimination of lead-tin solder based on the trace impurity analysis by ICP-AES.](#) *Anal Sci* 2003;19:415–8. [\[PubMed\]](#)
13. Suzuki Y, Kasamatsu M, Suzuki S, Ohashi K, Kawase A. Forensic discrimination of arsenous acid by the analysis of trace impurities with ICP-AES. *BUNSEKI KAGAKU* 2001;50(5):335–9.

Additional information and reprint requests:
 Masaaki Kasamatsu, M.Sc.
 National Research Institute of Police Science
 6-3-1 Kashiwanoha, Kashiwa city, Chiba 277-0882, Japan
 E-mail: kasamatu@nrps.go.jp