

## pH Indicators As Chemical Reagents for the Enhancement of Footwear Marks

**REFERENCE:** Glattstein, B., Shor, Y., Levin, N., and Zeichner, A., "pH Indicators As Chemical Reagents for the Enhancement of Footwear Marks," *Journal of Forensic Sciences, JFSCA*, Vol. 41, No. 1, January 1996, pp. 23–26.

**ABSTRACT:** Enhancement of weak two-dimensional shoemarks is often necessary due to the poor image detail. Thiocyanate is regarded in the literature as the most effective reagent for the chemical enhancement of footwear marks. In this study we have examined the possibility of using pH indicators, Bromophenol Blue and Bromocresol Green, as chemical reagents for the enhancement of footwear marks. The performance of these reagents on various surfaces, such as plastic sheets, brown paper, cardboard, porcelain bathroom tiles and cotton cloth, was compared to that of the thiocyanate reagent. It was found that these reagents were much more effective than ammonium thiocyanate for the samples of shoeprints in various regions of Israel. The mechanism of chemical enhancement of footwear marks by these reagents was elucidated. A solution of 1% Bromophenol Blue and 5% of water in methanol was chosen as the Bromophenol Blue formulation in this laboratory for the chemical enhancement of shoeprints.

**KEYWORDS:** criminalistics, shoemarks, footwear marks, chemical enhancement

In criminal investigations it is often necessary to enhance weak, two-dimensional, footwear marks. Various chemical reagents were reported as being effective for the enhancement of footwear imprints (1–4). Most of the proposed reagents were those used for the development of latent fingerprints, for instance small particles reagent (SPR), iodine, physical developer, etc. Some of these reagents were chelating agents for various cations (for example, Ca, Mg, Al and Fe) and others, such as ammonium or potassium thiocyanate, reagents for traces of ferric ion. Although calcium is the most abundant ion in soil water and road dust (23  $\mu\text{g}/\text{mL}$  and 17- $\mu\text{g}/\text{mL}$ , respectively) (4), only some enhancement was achieved with the 8-hydroxyquinoline chelating agent (for  $\text{Ca}^{+2}$  and other ions). Thiocyanate was the only reagent found suitable for use on mud and dust marks over all tested substrates (3,4). In this study we have examined the possibility of using the pH indicators, Bromophenol Blue (BPB) and Bromocresol Green (BCG), to enhance the footwear marks. Their performance was compared to that of thiocyanate. In order to elucidate the mechanism of the enhancement using these reagents, we carried out experiments to examine the pH changes occurring during their interaction with footwear marks residues.

<sup>1</sup>Scientific Officers and Head, respectively, Toolmarks and Materials Laboratory, Division of Identification and Forensic Science, Israel Police Headquarters, Jerusalem, Israel.

Received for publication 23 Sept. 1994; revised manuscript received 7 June 1995; accepted for publication 8 June 1995.

### Experimental Procedure and Results

The experiments for the enhancement of footwear imprints were carried out on the following substrates: white and brown paper, cardboard, cotton cloth, polyethylene plastic sheets and porcelain bathroom tiles. In order to compare any two methods of enhancement, the footwear marks on paper or on plastic sheet were cut in half and the two methods were applied, one on each half. In the porcelain bathroom tiles case, half of the shoeprint was sprayed while the other half was covered.

It should be pointed out that we did not observe any significant enhancement of footwear imprints (collected in various regions in Israel) with ammonium thiocyanate, in contrast to the results reported by Davis (3).

Bromophenol Blue is a pH indicator with a pH transition range of 3–4.6 (5). In its acidic form it is yellow and in its basic form it is blue. A solution of 1% Bromophenol Blue in methanol or in methylene chloride was sprayed on footwear prints on various surfaces. Usually, a blue color was developed immediately on a yellow background for all the tested substrates (Fig. 1), except for the case of the white paper where the background turned blue.

In some cases we found that the enhancement was quite weak. If the enhancement of the shoeprint was not satisfactory after spraying with the Bromophenol Blue solution, the print was exposed to water vapor using a boiling kettle. It was found that the exposure to water vapor may improve the enhancement significantly (Figs. 2, 3). The extent of exposure to the water vapor must be controlled carefully. If the exposure is too extensive, the background surface may be colored blue as well.

Bromocresol Green is a pH indicator with a pH transition of 3.8–5.4 (5). In its acidic form it is yellow and in its basic form it is blue. It was applied in a similar manner as the Bromophenol Blue and the results were also similar.

### Discussion

The conclusion that may be drawn from the enhancement experiments with Bromophenol Blue or Bromocresol Green is that the pH existing in the region of footwear marks was above the pH transition range of the indicators. Therefore a blue coloration was obtained there, and not on the background (except for the case of white paper), where the indicators remained in their acidic form (that is, below its pH transition range).

In order to assess the mechanism responsible for the above observation, several experiments were carried out. Since the shoemarks tested for enhancement were practically dust marks, the experiments were carried out on dust samples collected in the area of the laboratory and in various regions of Israel.

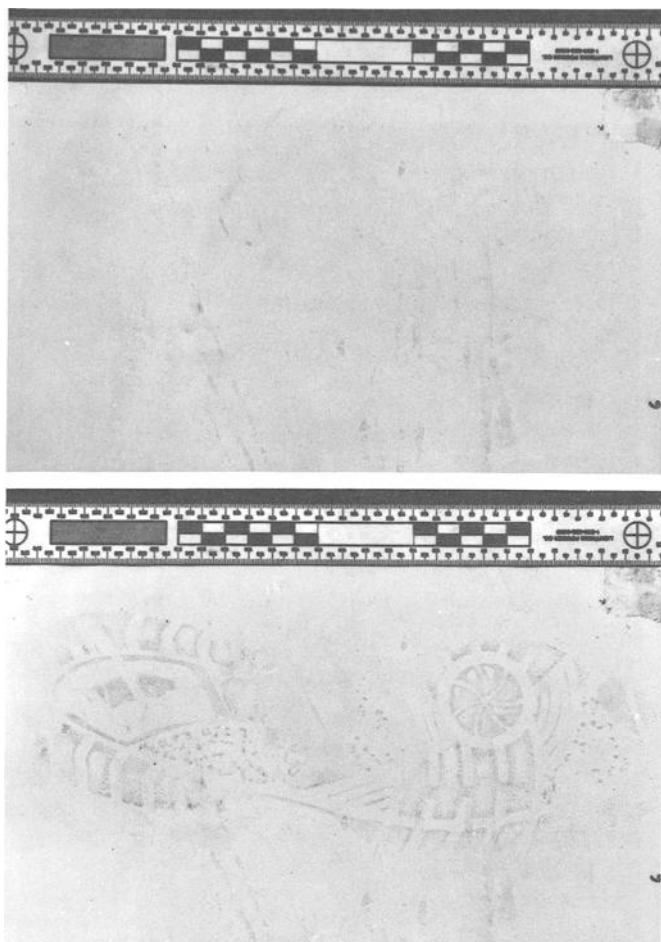


FIG. 1—A: Shoeprint before enhancement. B: Shoeprint after enhancement by Bromophenol Blue.

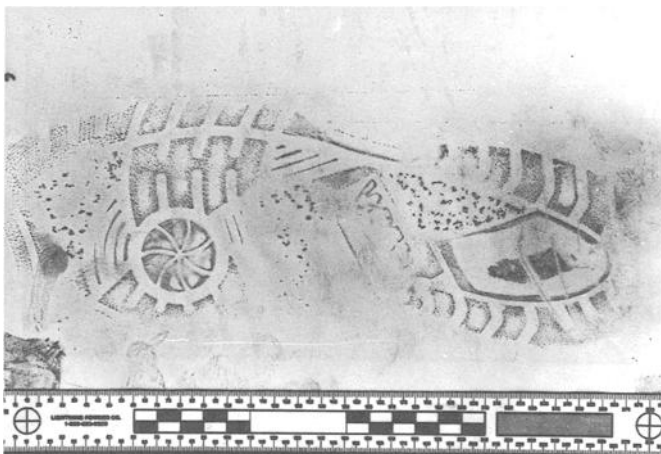


FIG. 2—Enhanced shoeprint (Fig. 1B) after exposure to water vapor.

First, suspensions of dust in water were prepared by mixing equal volumes of dust and distilled water. The measured pH (Hana Inst. 8520) of the water was about 6.5 and of the dust suspensions—6.2 (equilibration of half an hour).

We then carried out titrations of the Bromophenol Blue indicator with distilled water as follows: to 0.05 mL of the indicator in the

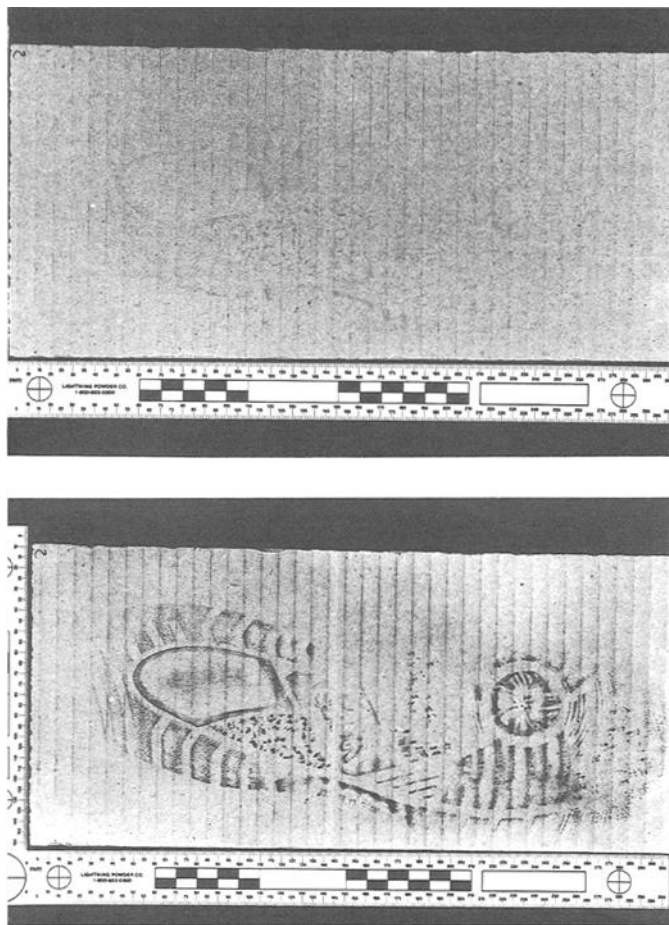


FIG. 3—A: Shoeprint on cardboard before enhancement. B: Shoeprint after enhancement and exposure to water vapor.

test tube we dropped distilled water while observing the color change of the solution. Only after addition of 1.5 mL water, a slight color change was observed from yellow—orange (the color of the indicator solution) to a red tint. Another 1.5 mL of water were necessary to change the color to purple—blue. These results show that in order to change the color of the 1% indicator solution, about a fifty times greater volume of water than indicator was necessary.

On the other hand, addition of only 2 mg of dust to 0.05 mL of the indicator solution caused a slight change to a blue tint. This is changed to a distinct blue color after addition of to the suspension of just 0.05 mL of water. The same results were obtained for all the dust samples.

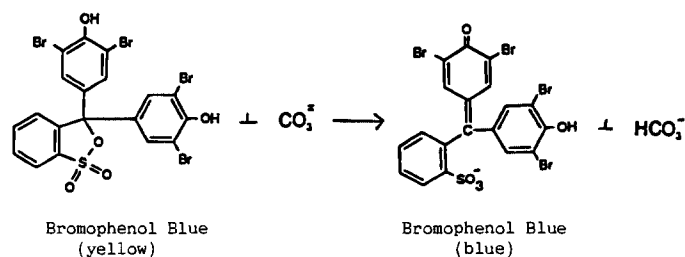
Another experiment of titration was carried out using the pH-meter as follows: 1 mL of water was added to 1 mL of 1% Bromophenol Blue in methanol. An orange red color was obtained and the pH of the solution was 0.9. To this solution we added dust from the laboratory while measuring pH until a color change to blue—purple was obtained. Table 1 presents the obtained results.

A plausible explanation for these phenomena is that a dust suspension in water has a much higher buffering capacity than water itself. Thus, even very small amounts of dust are sufficient to change the pH of the indicator solution above its pH transition range.

TABLE 1—Titration of BPB solution by dust.

Cummulative quantity of dust, gr.	pH	Color
0	0.9	Red-orange
0.36	2.4	Red-brown
0.9	3.6	Red brown
2.7	4.2	Blue-purple

Although general data of dust composition exists in the literature (4), we analyzed the dust samples we used (see for example Figs. 4, 5) using SEM/EDS (CamScan 3 SEM with a Tracor TN 5400 EDS system) and X-ray powder diffraction (Diano 8000 instrument) in order to substantiate the suspected buffering capacity of the dust. The main elements in dust as determined by SEM/EDS were Ca and Si and the identified compounds as determined by X-ray diffraction were calcite ( $\text{CaCO}_3$ ) and quartz ( $\text{SiO}_2$ ). The presence of carbonate was also confirmed by evolution of gas upon addition of dilute hydrochloric acid (5%) to the dust samples. Based on these results we carried out reaction with  $\text{CaCO}_3$  (analytical grade). BPB and water as with the dust samples and similar results were obtained. Obviously the buffer for acid in this case is the carbonate anion according to the reaction:



This may also explain the blue background coloration obtained on a white paper upon applying BPB, since it is known that  $\text{CaCO}_3$  serves as a filler in paper (6). In brown paper a blue coloration of the background was not observed because the concentration of Ca in it was found to be very low (Fig. 6), while in white paper a high concentration of Ca was found (Fig. 7). Applying dilute hydrochloric acid on a piece of a white paper also caused evolution of gas indicating presence of carbonate while in the case of a brown paper no reaction was observed.

We also carried out the same reactions (as with the dust and  $\text{CaCO}_3$  samples) with samples of clays: kaolinite  $\{\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}\}$ , illite  $\{\text{KAl}_2(\text{OH})_2[\text{AlSi}_3(\text{O},\text{OH})_{16}]\}$  and montmorillonite  $\{(\text{Mg},\text{Ca})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 4\text{H}_2\text{O}\}$  (7). Only with montmorillonite a transition to a blue color occurred similar to that of  $\text{CaCO}_3$  and the dust samples. However the clays' concentration in all the examined dust samples seems to be low, based on a low concentration of aluminum (Figures 4 and 5). Therefore the clays cannot contribute significantly to the color transition of the pH indicators in the examined dust samples.

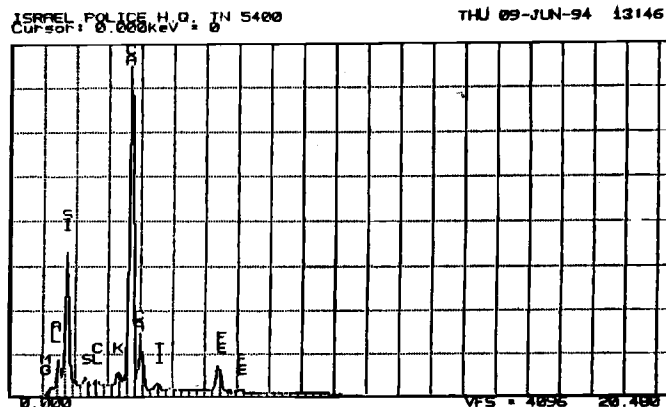


FIG. 4—EDS spectrum of dust sampled from the area of the laboratory, central region of Israel.

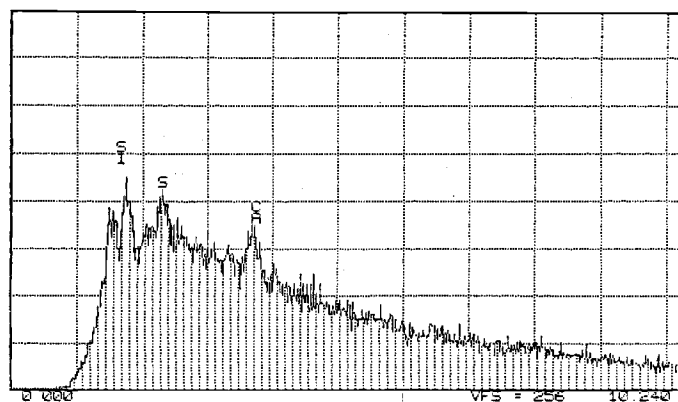


FIG. 6—EDS spectrum of a brown paper.

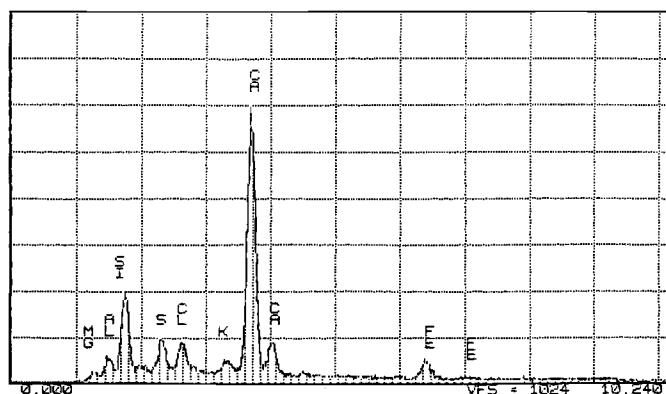


FIG. 5—EDS spectrum of dust sampled from the northern region of Israel.

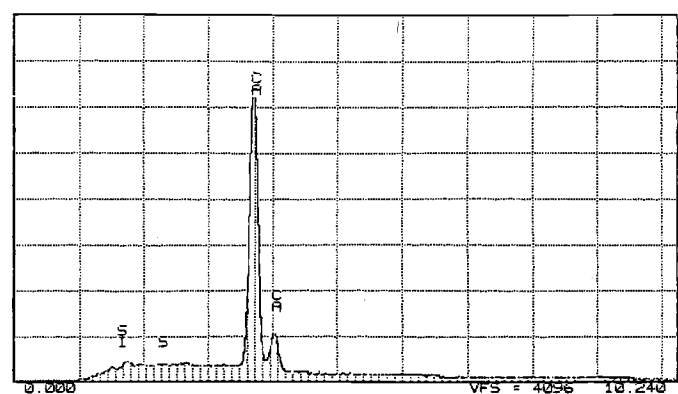


FIG. 7—EDS spectrum of a white paper.

Probably the role of water in the pH transition is to provide a medium for a quick equilibrium with respect to pH. Therefore, exposure to water vapors is necessary apparently when the shoeprints are quite dry, in order to achieve maximum color enhancement following spraying with the Bromophenol Blue or Bromocresol Green solutions.

The following experiments verified this assumption:

Shoeprints on plastic sheets and paper were kept for an hour in an oven at a temperature of 80°C in order to dehydrate the dust traces forming the shoe prints. Immediately after taking the shoeprints from the oven, they were sprayed with the Bromophenol Blue reagent. A weak blue coloration was developed which was enhanced significantly by exposure to water vapors. In additional experiments, solutions of 1% Bromophenol Blue in methanol mixed with various amounts of water were prepared and sprayed on the shoeprints after heating them in the oven and the development of the distinct blue color on the prints was immediate as in the case of exposure to water vapors.

We found that too much water in the Bromophenol Blue spray (e.g., 90% water and 10% methanol) causes blue coloration of the background as well and not only of the shoeprint. Good results were obtained with low concentration of water in the formulation. A solution of 1% Bromophenol Blue and 5% of water in methanol was chosen as the Bromophenol Blue formulation in this laboratory for the chemical enhancement of shoeprints.

There are other pH indicators (8) that have a pH transition range that could be suitable, in principle, for the chemical enhancement of footwear marks. However, except for Bromochlorophenol Blue which has a similar transition color to Bromophenol Blue and Bromocresol Green, other indicators in this range have less favorable color changes and therefore were not been examined.

### Conclusion

pH indicators, Bromophenol Blue and Bromocresol Green reagents, were examined in this study for the chemical enhancement of footwear marks. We have found that both reagents were

much more effective than ammonium thiocyanate on the dust shoeprints collected in Israel. Obviously the potential of the pH indicators as reagents for the chemical enhancement of shoeprints should be assessed for every environment and environment since it will depend on the composition of the dust in that area.

### Acknowledgments

The authors would like to express their thanks to superintendent E. Springer, of the Division of Identification and Forensic Science, for his help in preparing this manuscript and to A. Sandler, of the Geological Survey of Israel, for providing us with the clay samples.

### References

- (1) Bodziak WJ. Footwear impression evidence. Elsevier Science Publishing Co. Inc., New York, Amsterdam, London, 1990.
- (2) Cassidy MJ. Footwear identification. Canadian Government Publishing Center, Quebec, 1980.
- (3) Davis RJ. A systematic approach to the enhancement of footwear marks. *Can Soc Forensic Sci J* 1988;21:98-105.
- (4) Keedwall E, Birkett J, Davis RJ. Chemical methods for the enhancement of footwear marks, MPFSL Report No. 73, 1988.
- (5) Weast RC. Handbook of Chemistry and Physics. 1st Student Edition, CRC Press, Inc. 1987;D-89.
- (6) Brunelle RL. Questioned documents examination, in: Saferstein, R., ed., "Forensic Science Handbook," Prentice-Hall Inc., 1982;719.
- (7) Kerr PF. Optical mineralogy, third edition, McGraw-Hill Book Company, Inc., 1959;408.
- (8) Bishop, E., "Indicators," Pergamon Press, 1970;79-80, 87, 93-5.

Address requests for reprints or additional information to:  
Baruch Glattstein, M.Sc.  
Division of Identification and Forensic Science  
Israel Police Headquarters  
Jerusalem 91906, Israel.