

## TECHNICAL NOTE

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# The Accelerated Polyvinyl-Alcohol Method for GSR Collection—PVAL 2.0

**REFERENCE:** Schyma C, Placidi P. The Accelerated polyvinyl-alcohol method for GSR collection—PVAL 2.0. *J Forensic Sci* 2000;45(6):1303–1306.

**ABSTRACT:** The polyvinyl-alcohol collection method (PVAL) is used in forensic practice to gather topographical information about gunshot residues (GSR) from the hands to decide if the subject has made use of firearms. The results allow a distinction between suicide and homicide. The only inconvenience of PVAL was that the procedure took about 60 min because three layers of liquid PVAL had to be applied and dried. Therefore, the collection method was only applied to corpses. The improved and accelerated PVAL 2.0 uses a sandwich technique. Cotton gauze for stabilization is moistened with a 10% PVAL solution. A solid film of PVAL (Solublon<sup>®</sup>) is spread on the cotton mesh. The gauze is then modeled to the hand and dried with a hair dryer. After removing the cotton gauze, the traces are embedded in the water-soluble PVAL. The procedure does not take more than 15 min. The results demonstrate the qualities and advantages of PVAL: topographical distribution of GSR, highest gain of GSR, sampling of all other traces like blood, backspatter etc., and humidity does not reduce the gain. In addition, with the new PVAL 2.0 dislocation of GSR or contamination are excluded. PVAL 2.0 can also be applied on live suspects.

**KEYWORDS:** forensic science, criminalistics firearms, gunshot residues, bloodstains, polyvinyl-alcohol, homicide, suicide

Investigation of violent deaths due to firearms is a common task for law enforcement and medical examiners. Both contribute to the distinction between suicide and homicide by autopsy findings and trace evidence. The discharge of a firearm deposits gunshot residues (GSR) on the hand holding the weapon (1). GSR consist of myriads of particles containing vaporized and condensed metals from the primer and the bullet like lead, barium, antimony, and zinc etc. (2). Most of the particles measure less than 1  $\mu\text{m}$ , but some reach up to 100  $\mu\text{m}$  (3). The larger particles (over 1  $\mu\text{m}$ ) are blasted onto the surfaces surrounding the firearm like the hand holding the weapon. Therefore, the shooter's hand can be identified by the density distribution of GSR on his hands (4). In addition, if the gunshot wound is self inflicted, there are often biological traces caused by backspatter like blood and tissue found on the hand (5). Principally,

there are two ways of sampling GSR on the hands: 1) Cumulative methods: cotton-swabs for bulk analysis or tape lifts for scanning electron microscopy, and 2) Topographic sampling: adhesive foils, latex, or polyvinyl-alcohol (PVAL). But it is not obvious that all methods give positive results of GSR in all suicide cases (6,7). The method with the most gain (percentage of particles collected of the total number) of GSR is the PVAL method. The water-soluble liquid polymer is dotted and painted in three layers on each hand. All the layers must be dried with a hair dryer. In the last layer, a medical gauze is embedded to stabilize the "glove." The PVAL method has been applied in forensic practice for several years and provides excellent results (8). The only inconvenience of this sampling method is the time of more than one hour that is needed for collection, therefore, the method was restricted to corpses. Research was needed in forensic medicine to find a faster method to gather GSR with the performance characteristics of PVAL and this led to the development of the PVAL 2.0 method.

### Material and Methods

The following materials are necessary:

- Polyvinyl-alcohol (Sigma P 8136) as a 10% solution in 20% ethanol
- Solublon<sup>®</sup> KL#40, water-soluble PVAL-film 40  $\mu\text{m}$  thick (Aicello Company)
- Medical cotton gauze
- Plastic kitchen board with juice groove (at least 10 in.  $\times$  8 in.), plastic smoother, hair dryer, and new fine paintbrush

### Procedure

A piece of 9 in.  $\times$  6 in. of cotton gauze is spread out on the kitchen board (Fig. 1). A few milliliters of the PVAL solution are poured on the cotton mesh (Fig. 2). The liquid is spread over the surface using the smoother until the gauze is just moistened (Fig. 3). The Solublon<sup>®</sup>-film is cut to the required size (approximately 8 in.  $\times$  6 in., depending on size of the hand) and put on the wet cotton (Fig. 4). A few seconds later, the Solublon<sup>®</sup>-film begins to dissolve. The cotton gauze is grasped at the borders, removed from the board (Fig. 5) and applied on the back of the subject's hand, the Solublon-side turned to the skin. It is important to model the form of the hand tightly, especially thumb and index finger. Missing parts are covered using patches (Fig. 6) prepared as described. If some areas do not adhere on the hand, they are painted with a little liquid PVAL.

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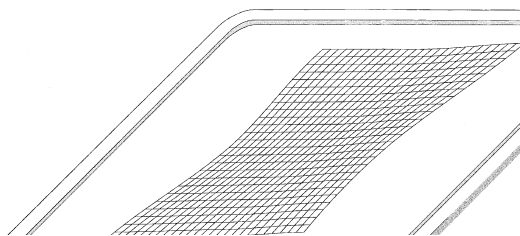


FIG. 1—Cotton gauze is spread out on the kitchen board.

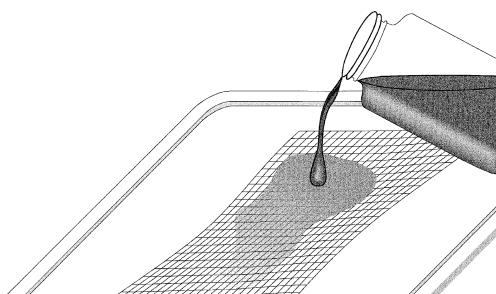


FIG. 2—PVAL solution is poured on the cotton mesh.

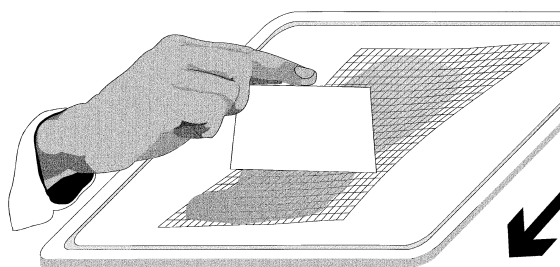


FIG. 3—PVAL liquid is spread using a smoother.

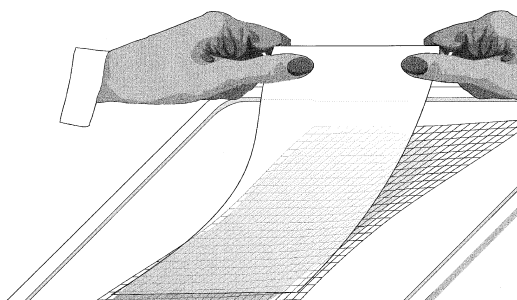


FIG. 4—Solublon®-film is put on the wet cotton.

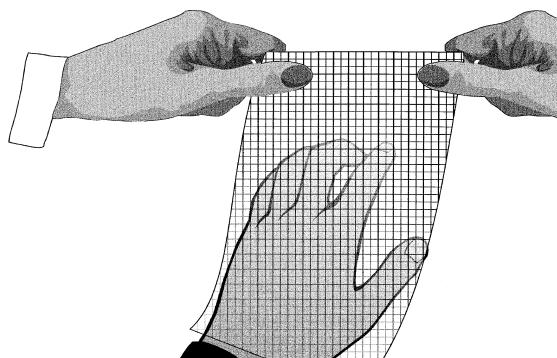


FIG. 5—The cotton gauze taken at the borders is applied on the back of the hand, the Solublon-side turned to the skin.

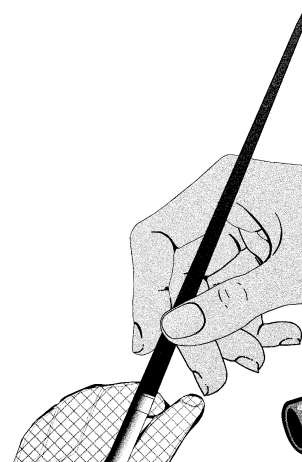


FIG. 6—The hand is modeled tightly. Missing parts are covered using patches (arrow) and liquid PVAL. Dry for 5 to 7 min with the hair dryer and 3 min in situ.

After modeling the hand has to be dried with a hair dryer for about 7 min. Good ventilation is important, an excess of heat has to be avoided. The wet cotton mesh appears transparent, whereas the dried cotton recovers the original white color. The “glove” can be removed after another 3 min of naturally drying in situ (Fig. 7).

### Results

The PVAL 2.0 method was first used in experimental conditions. GSR were sampled on the shooter’s hand after one or several shots. The calibers .22 long rifle, .32 Browning, 9 mm Luger, and .38 special were examined with full jacketed ammunition and round-nose lead bullets. The primers contained lead, barium, and antimony. The PVAL-gloves were first radiographed with a Faxitron M55 (Hewlett-Packard) on high-resolution industrial X-ray film Agfa D3. The tension was set to 50 kV. The microfocuss X-ray-tube gave high-resolution images of the distribution of the GSR. The PVAL-gloves were then treated with 2% tartaric acid and sodium rhodizonate solution. Red and purple colored GSR were easily detected with a stereo microscope Stemi 2000 C (Zeiss) at 20 to 40 fold magnification. The traces were found embedded in the PVAL-matrix so that the particles were durably preserved. The treatment with indicator liquids did not cause a loss of trace material, as occurred regularly with adhesive films. Finally the colored particles were analyzed using an Eagle  $\mu$ -Probe II (Röntgenanalytik Messtechnik, 65232 Taunusstein-Neuhof, Germany). This X-ray microbeam

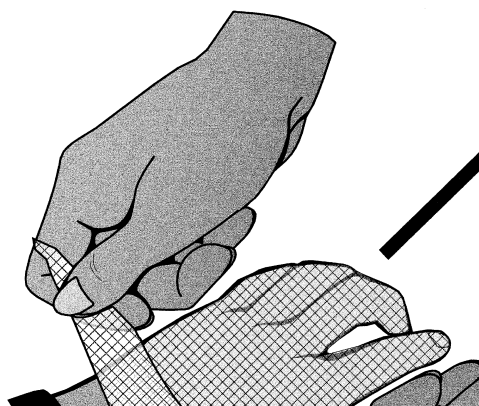


FIG. 7—The “glove” is removed, pulling it from up to the fingers.



FIG. 8—Right glove of a shooter's hand with blood on the middle finger. Suicide with a pistol .22 long rifle in caliber.

spectrometer analyzes the characteristic X-ray emission of a sample which is excited by X-rays focused on an area of only 100  $\mu\text{m}$  (microfocus EDX, energy dispersive X-ray fluorescence). The entire PVAL-piece was placed in the great sample chamber without preparation and positioned by a motorized X-Y-Z-stage. Then the region of interest was mapped. Figure 8 shows the right glove of a suicide with a .22 lr pistol. Two examples of micro EDX analysis with the Eagle  $\mu$ -Probe II of this case are given in Fig. 9.

In order to estimate the gain of the PVAL 2.0 method two series of test shootings were performed with a 6 in. barrel revolver (Taurus, Brazil) .22 long rifle in caliber. The shooter washed his hands and the weapon was cleaned before each shot. After one shot with the right hand first a PVAL-glove was taken from the hand, after this the remaining traces were collected using aggressive adhesive films (Filmolux<sup>®</sup> S23, Neschen, 31675 Bückeberg, Germany). In the second series the order was inverted: first GSR were collected with Filmolux<sup>®</sup> adhesive films from the hand, after this the PVAL 2.0 method was applied. Two regions of interest were analyzed, the index (5  $\text{cm}^2$ ) and the back of the hand (20  $\text{cm}^2$ ). Table 1 gives the results of the relation of the particles found by both methods.

After the application of the polyvinyl-alcohol method only few traces remained on the hands. The results with adhesive films however varied strongly in dependence of humidity and grease on the skin.

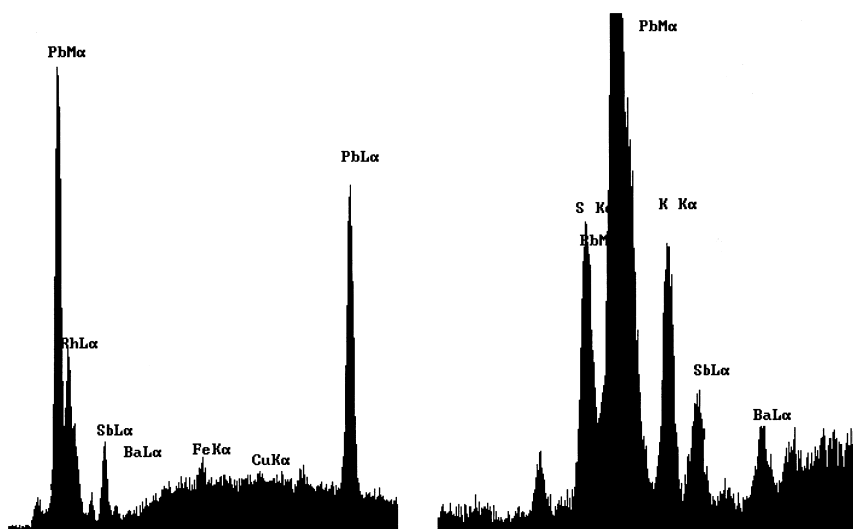


FIG. 9—Spectra of GSR particle groups analyzed on a microspot (100  $\mu\text{m}$ ) with the Eagle  $\mu$ -Probe II in the PVAL of the suicide with a pistol .22 long rifle in caliber. Time of measurement each 100 s. Direct EDX analysis of red colored particles without other preparation.

TABLE 1—Comparison of the gain of the topographic collection methods PVAL 2.0 and Filmolux adhesive films. Percentage of particles found by one method of the total number of GSR > 1  $\mu\text{m}$ .

Region	Index Finger		Back of the Hand	
First series of shooting (.22 lr)	First collection with PVAL	Second collection with adhesive film	First collection with PVAL	Second collection with adhesive film
Minimum	86%	14%	90%	10%
Maximum	94%	6%	96%	4%
Second series of shooting (.22 lr)	First collection with adhesive film	Second collection with PVAL	First collection with adhesive film	Second collection with PVAL
Minimum	7%	93%	9%	91%
Maximum	75%	25%	50%	50%

The PVAL 2.0 method was applied for the first time in forensic practice in the case of a suicide with a 9 mm Luger pistol (cartridge Sellier&Bellot, full metal jacket). The new PVAL-glove sampled not only the typical GSR but also embedded the bloodstains on the right hand of the deceased. Microradiography revealed gunshot residues and macropatter of tissue and bone fragments within the bloodstains. Since then several cases of suicide and one homicide were successfully examined with the new method. In all cases wet and/or dried bloodstains were embedded in the PVAL-matrix without any problem.

## Discussion

The problem of the classic polyvinyl-alcohol method was the minimum collection time of 60 min. This time was needed to apply and dry three layers of the liquid polymer. The hope was to reduce the procedure to a single layer. However, the quantity of PVAL in one layer was not sufficient to embed the gunshot residue particles in a film. The combination of solid (Solublon<sup>®</sup>) and liquid PVAL in a sandwich technique allowed the simultaneous application of all layers, followed by a single drying process. In contrast, the use of a Solublon<sup>®</sup>-film alone, moistened with distilled water could remove traces from the hand but was not resistant to laboratory analysis and handling.

The new procedure does not take more than 15 min. Thus, PVAL 2.0 is four times faster than the classic method. The results show the same qualities—embedding of all kinds of traces particularly bloodstains in their topographic distribution, and rich gain of trace material (over 85%) as in the past.

There are many techniques for sampling gunshot residues on hands. The topographic methods have the advantage over the cumulative procedures in that they give a pattern of GSR distribution. This makes it possible to distinguish if someone fired a gun or only handled it, if he was exposed to GSR as bystander, or by making defensive movements with his hands. To our knowledge, the PVAL-method is till now the most reliable topographic GSR sampling method in forensic practice. That was demonstrated combining both methods, PVAL, and adhesive films. The new PVAL-method gave rather uniform results. If PVAL was applied first, only 4 to 14% of the particles remained on the hand. If, however, adhesive films were used first, a large portion of GSR was only found with PVAL as second method (Table 1). The reliability of adhesive films was reduced by the particular condition of the hand, especially by humidity and grease. The brand of adhesive films (e.g., Scotch<sup>®</sup> 800 or Filmolux<sup>®</sup>) had little influence on the reliability of the method.

Compared with adhesive films PVAL removes much more trace material and works as well on moist hands (8). The experiences with latex are not sufficient for a comparison with polyvinyl-alcohol, but PVAL has the undeniable advantage that it is water soluble. Therefore, moist or dried bloodstains are embedded in the PVAL-glove preserving their original form and pattern. DNA-PCR analysis can be performed at any later date after GSR detection (9).

The examination of PVAL is regularly performed with three independent methods:

- Chemical indicators and stereo microscopy
- Microfocus X-ray imaging with the Faxitron M55 (Hewlett Packard)
- EDX analysis with the MESA 500 (Horiba, Kyoto) or the Eagle  $\mu$ -Probe II for higher sensitivity (Röntgenanalytik Messtechnik, Tausenstein)

Scanning electron microscopy (SEM) with energy dispersive X-ray

analysis (EDX) is also possible with previous PVAL and PVAL 2.0, but the Eagle  $\mu$ -Probe II offers an interesting alternative because the PVAL-glove can be directly analyzed without preparation or destruction.

The common advantages of the classic PVAL and the PVAL 2.0 method are:

- Image of the topographic distribution of GSR
- Higher gain of GSR as adhesive films
- Sampling of all kinds of traces: GSR, blood, backspatter, fibers, and hairs, etc.
- Humidity problems are neutralized
- Water-soluble matrix: application of classic chemical indicators is possible

With the improved and accelerated PVAL 2.0, there are three other advantages over previous PVAL:

- Dislocation of GSR is excluded—In the classic PVAL method the first layer must be dotted. Therefore there was the danger of a dislocation of GSR particles by the paintbrush. Only after drying the GSR were fixed on their place. The new method embeds the particles directly into the gel good Solublon<sup>®</sup>-film.
- Contamination is excluded—In the first layer of the previous PVAL method, the whole hand was worked with a paintbrush. In this procedure the paintbrush was dipped into a small bowl of liquid PVAL again and again. A contamination with GSR was theoretically possible by the liquid PVAL. Therefore, it was strictly prescribed for classic PVAL to use one paintbrush and bowl for each hand and to throw away the paintbrush after first use. The PVAL 2.0 method avoids all contact between GSR and liquid PVAL. Liquid PVAL is only applied outside the Solublon<sup>®</sup>-film to stabilize patches.
- Application on apprehended suspects is possible due to the reduced collection time.

The PVAL 2.0 method is the first choice for GSR sampling in all cases where the hands are wet, bloody or dirty, and is recommend in other difficult situations.

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