# DETECTION OF GUNSHOT RESIDUE CHEMICAL COMPONENTS BY MICROCRYTALLINE TESTS

Thiti Mahacharoen [1]

## Abstract

This research studied and differentiated chemical properties of gunshot residue (GSR) by using a microcrystal technique with three reagents: Sulfuric acid, Oxalic acid and Potassium Iodide. This technique is also implemented as a valuable and relatively fast tool to examine and detect gunshot residue by using a Polarized Light Microscope (PLM) to distinguish chemical and optical properties of Antimony (Sb), Barium (Ba) and Lead (Pb). The weapons used in this study are a .38 mm revolver pistol and a 9 mm semi-automatic pistol.

The results showed that GSR crystals occurred at a close range of shooting distance (less than 6 inches). For distances of 18 inches and further, fewer crystals formed and they were smaller in size. This is consistent with the theory of GSR existence varying at different shooting ranges. Different reagents and concentrations were specific for each element of GSR to lead to different crystal habits. This technique is an effective, fast, and inexpensive method of detecting each GSR element (Sb, Ba and Pb) and it is an effective technique for use in a laboratory or other forensic science unit with limited resources.

**Keywords**: Microcrystalline, Gunshot Residues, Polarized Light Microscope (PLM)

## 1. OBJECTIVES

1.1 To study the properties and morphology of gunshot residue microcrystal elements Antimony (Sb), Barium (Ba) and Lead (Pb) using 2 types of pistol, a revolver and a semi-automatic Glock pistol. at 3 different shooting distances of contact, 6 inches, and 18 inches, using the microcrystalline technique.

1.2 To test the sensitivity and determine proper concentrations of a testing reagent for a microcrystalline reaction of Antimony (Sb), Barium (Ba) and Lead (Pb).

## 2. LITERATURE REVIEWS

### 2.1 Gunshot Residue

Shooting a bullet from a firearm will cause the burning of the gap and powder charge. The burning part is called the Gunshot Residue or GSR. This will include a portion of the burnt and unburnt part, and maybe part of the metal bullet head remains. Part of the inorganic elements consist of barium (Ba), Antimony (Sb) and lead (Pb), and elements of the ignition part are composed of the nitroglycerin, stabilizer,

[1] Faculty of Forensic Science, Royal Police Cadet Academy, Email: thiti@rapc.ac.th
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which are Diphenylamine (DPA) and Ethyl Centralite (EC). These compounds remain on the shooter's hand for several hours depending on the activity of the shooter after shooting. The residual part of this ammunition can be used to inspect the type of ammunition. (Dalby et al, 2010).

The three main elements of the priming mixture of a cap are composed of Barium, Antimony, and Lead. These elements can be detected for gunshot residue analysis on a shooter's hand or at a target. These elements are found in combination in a bullet as follow (Schwoeble and Exline, 2000)

2.1.1 Initiator: The self-ignited part of the firing pin. The main chemical component is Lead Styphnate [$PbC_6H(NO_2)_3O_2$]

2.1.2 Oxidizer: The oxygen supplier of fuel and initiator. The Oxidizing Agent is Barium nitrate ($Ba(NO_3)_2$)

2.1.3 Fuel: The source for the ignition process. The chemical component is Antimony Sulfide ($Sb_2S_3$)

## 2.2 Polarized Light Microscope

A polarized light microscope is a special tool that can be used for viewing crystals. It can also be used to view skeletal muscle cells, collagen fibers (Collagen Fiber) cells, rods and cones, etc. (Chutanich, 2546) When observing an object, you can learn more about the details than with other types of camera, even if the lighting is correct. When a picture of the subject is taken, it will be shown and brighter. The principle of this camera is similar to that of a conventional lens camera, only the interior is equipped with a transverse or cut-off polarized disc, which is the first block between the eyepiece and the objective lens. The second sheet blocks the light between the lens and the object, so the camera can be used to find the two refraction or birefringence of the object (Petraco and Kubic, 2004).

This two-way refraction relies on the arrangement of the structure, which is too small to be observed with a conventional microscope lens. This type of camera comprises first of a Nicol Prism or two polaroid filters, under the light lens. This is called the Polarizer and acts as a microscope to work in the same direction (Plane Polarized Light) as the second prism which is placed between the objective lens and the eyepiece lens. The Analyzer is rotated until the perpendicular axis to the polarizer has no light passing through the eyepiece lens, causing a dark field effect. If the sample is isotropic or has a single fracture (Singly Refractive) it remains visible, black in the field of view. However, if the sample has a sort of molecular structure, the two-way or anisotropic will see the structure illuminated in the dark area (Bloss, 1999)

In the early years, this type of camera was used in geology to inspect various crystalline stones. In biology, it was used to observe polymers such as starch, urea, and biological macromolecules. Later, it was applied to use in medical applications, marine science, material sciences, food science, and forensic science; for example, when looking at monosodium urate, muscle tissue, minerals, fatty fibers. It was also used to look at ceramics, glass, and metals (Faculty, Department of Biology and Botany, 2553)

Birefringence is the difference between the refractive index in a fiber calculated from retardation (r) and thickness (T) with the formula B (birefringence) = r (nm)/1,000 T (m).

The Becke Line Method is a method to find the comparative refractive index compared with the medium. It is a bright halo line. When the focus is moved upward the Becke line will move into the medium with a higher refractive index

Interference Colors are colors from light which is out of phase and can be observed as crossed polar. The retardation can be found using the Michel-Lévy chart.

The Michel-Lévy Chart is a diagram showing the relationship of interference color, thickness of a sample, and birefringence

Isotropic Materials are materials that have identical values of a light property in all directions. Glass, metals, and liquids are examples of isotropic materials. There is a single value on the refractive index.

Anisotropic Materials are materials that have different values of light property. There is more than one value of refractive indices splitting one light ray into two rays, vibrating perpendicular to each other.

Plane Polarized Light is a light ray with one plane of vibration.

Pleochroism is the light property of an object that gives a different color when using polarized rays.

Privileged Direction (of a polarizer) is the direction of vibration when light passes through a Polarizer.

The Refractive Index is the value of the refractive index of fibers against the refractive index at which the fibers are located.

Retardation (r) is the distance between the two rays when moving through an object with a refractive index of two values (Anisotropic Material)

Sign of Elongation is the value of the fiber. If the fibers have a refractive index in the long side of the fiber more than the width's, the sign of Elongation is positive. If it is less, it will be a negative value.

### 2.3 Microcrytal Techniques

The Microcrystal test is a method that can be clearly observed. This test is a study of the development of the crystal habit. The amorphous characteristics of formed crystals are unique and have a different crystalline shape in each element. The reactive compounds (Reagent) used in the test can be taken to form the appearance of crystalline patterns. Clothes of a suspects can be examined for gunshot residue. This test is quick, accurate, and ideal for any laboratory that does not possess high-priced verification tools such as SEM or AAS instruments. The growth of crystalline molecules can have both physical and chemical dependency. With the microcrystalline test, results are highly specific and precise. While observing the crystal, the expert will monitor the shape of the crystals. The comparison of samples is highly specific. This method can also be used to confirm results in the courtroom

### 2.4 Related Research

Kamchai Sritham (2554) studied the elemental quantities of gunshot residue from a gun on gloves after shooting at different times with the SEM machine. After firing, a resulting grease is caused by the integration of Pb, Sb and Ba, placed in a primer, as a component of ammunition, when the gun fires, causing explosion at high temperatures. The combination of elements and use of SEM will display particle granules.

The collection of GSR is done by using the stub. This is a carbon-sticky adhesive tape which is exposed to the position where the trace is shown after shooting, such as a palm, face, or clothing. A suspect's sample is usually present for not more than 12 hours on a living person, and usually not to more than 24 hours if the person is dead. The study used 3 bullet sizes: 9 mm, .45, and shotgun gauge 12 and durations of 1 month, 6 months, and 1 year. This was to examine whether different times and sizes of ammunition would affect the detection of metal particles after shooting using SEM.

Kevin et al. (2000) Studied γ-Hydroxybutyric (GHB) classification by the microchemical method using reactive compounds (Reagent) Cupric Nitrate and Silver Nitrate 0.1 g dissolved in 10-ml crystalline of GHB. Rectangular when doing a test using reactive compounds (Reagent) Cupric Nitrate and Silver Nitrate found that there were no crystals with other drugs, including biological drugs similar to GHB.

Mathieu et al. (2008) studied the microcrystalline test to optimize γ-hydroxybutyric (GHB) using reactive compounds (reagent) Silver Nitrate or Copper Nitrate and found that Silver Nitrate or Copper Nitrate is a reactive substance (reagent) that can be seen as a large crystalline. Reagent Silver Nitrate or Copper Nitrate are highly specific for testing. Γ-Hydroxybutyric (GHB), however, the reactive compounds (Reagent), Silver Nitrate or Copper Nitrate are not suitable for the testing of Hydroxyl Acids substances such as Glycolic Acid, although the crystals have a similar crystalline structure, which in the test of γ-Hydroxybutyric (GHB) and similar biological compounds. The selection of reactive compounds (Reagent) for test use is very important because it is used in the crystallization of γ-hydroxybutyric (GHB).

Nelson et al. (2011) studied microcrystal analysis of Cocaine Hydrochloride and the addition of additives was also studied to test the tendency of changing the morphology characteristics of crystals. the tendency to change the morphology characteristics of cocaine found in caffeine, Lidocaine HCl, Procaine HCl, Levamisole HCl, and baking soda was looked at. It was found that crystallization depends on the concentrations. The test showed a reduction in the error of blocking the contamination of the crystallization. This is another useful laboratory analysis tool.

Leonie et al (2011) studied 4-methylmethcathinone (mephedrone), benzylpiperazine (BZP) and 5,6-methylenedioxy-2-aminoindane by using Mercury chloride and found that with each compound when using a high specific reagent, a crystal is formed, so the Microcrystalline technique can show a positive result of BZP and caffeine without other contaminations.

Mahacharoen (2012) developed a microcrystalline technique to examine the propoxephene derivatives combined with the Attenuated Total Reflection (ATR) technique to confirm the validity of the method. The results showed that this technique can differentiate the two analogues effectively and can be applied to test the derivatives of propoxephene.

Silletti (2015) developed a microcrystalline test in clonazepam, finding that filling acetone or chloroform mixed with reactive compounds (reagent) 10% Platinum Chloride had a result of Clonazepam crystals characterized by colorless in the

Rosettes Blunt-Ended Rods. Although Platinum Chloride is a conventional reagent, the result showed that other drugs do not have the same reaction to the reactive compounds (Reagent). This test is an effective method that can be used in forensic laboratories.

Therefore, this microcrystalline technique is a method which can be developed and precisely applied to the detection of gunshot residue elements. It has a fast detection rate and is suitable for laboratories with low cost unlike using other more complicated and expensive techniques such as the Scanning Electron Microscope or the Atomic Absorption technique.

## 3. MATERIALS AND METHODS

This is experimental research to study the morphological characteristics and the appearance of the of the crystal habit of the three main elements of gunshot residue, including how Antimony (Sb), barium (Ba) and lead (Pb) reacts with three types of reactive reagent (KI), Oxalic Acid ($C_2H_2O_4$) and Sulfuric Acid ($H_2SO_4$), using the microcrystalline method, with a microscopic technique that uses a single-plane oscillating light microscope (Polarized Light Microscope) as a tool to characterize crystals. The characteristics of each type of crystals can be distinguished from each other and used to identify the type of gunshot residue for forensic application and investigations.

### 3.1. Materials

3.1.1 Three standard solutions which are 1000 mg/L of $Ba(NO_3)_2$, $Pb(NO_3)_2$ and $Sb(NO_3)_2$

3.1.2 Potassium Iodide (KI), Oxalic Acid ($C_2H_2O_4$), Sulfuric Acid ($H_2SO_4$) and Nitric Acid ($HNO_3$)

3.1.3 Polarized Light Microscope (PLM)

3.1.4 Microscope slide

3.1.5 Forceps

3.1.6 Dropper

3.1.7 Glock .38 revolver pistol

3.1.8 Glock 9 mm semi-automatic pistol

3.1.9 non sterile rubber glove

3.1.10 non bleached cotton fabric for shooting target

### 3.2 Sample collection and shooting

3.2.1 shooting a bullet from a revolver and semi-automatic pistol at three distances: contact, 6 inches and 18 inches to cotton fabric target

3.2.2 collecting gunshot residue from a cotton fabric by using 5% nitric acid

3.2.3 taking dissolved solution for microcrystalline technique by reacting with prepared reagent and observing the crystal formation with Polarized Light Microscope

### 3.3 Sensitivity testing and determination of proper concentration of testing reagents

3.3.1 $Ba(NO_3)_2$, $Pb(NO_3)_2$ and $Sb(NO_3)_2$ standard solution preparation at 100,200,300,400 and 500 mg/L by pipetting standard solution 10, 20, 30, 40 and 50 mL consecutively in 100 mL Erlenmeyer flask with distilled water and add to 100 mL total volume.

3.3.2 reagent preparation

3.3.2.1 For 5% KI, dissolved 1 g of KI in 20 mL distilled water and use stirring rod for dissolving solution

3.3.2.2 For 10% KI, dissolved 1 g of KI in 10 mL distilled water and use stirring rod for dissolving solution

3.3.2.3 For 5% Oxalic Acid, dissolved 1 g of Oxalic Acid in 20 mL distilled water and use stirring rod for dissolving solution

3.3.2.4 For 10% Oxalic Acid, dissolved 1 g of Oxalic Acid in 10 mL distilled water and use stirring rod for dissolving solution

3.3.2.5 For 5% Sulfuric Acid, pipetting 5 mL of 98% sulfuric acid and dilute with 100 mL distilled water and use stirring rod for dissolving solution

Three types of standard solutions are $Ba(NO_3)_2$, $Pb(NO_3)_2$ and $Sb(NO_3)_2$ with concentrations of 100, 200, 300, 400 and 500 mg/L using 3 types of reagent, including Sulfuric Acid, Oxalic Acid and Potassium iodide, repeated 5 times for each sample to the test sensitivity and find the optimum concentration of the reaction (Reagent) with the Microcrystalline technique by dropping 10 µL of each testing solution on a glass slide. 10 µL of a regent is then added to the same glass slide near the testing solution. A toothpick is then used to drag the testing solution into the reagent. The optical properties are then observed under the Polarized Light Microscope. Adjusting image magnification to 200X, the characteristics and color appearance of the crystals are recorded.

### 3.4 Microcrystalline testing of gunshot residue

The experiment used two types of gun: revolver and semi-automatic pistol, at three different shooting ranges: contact, 6-inches, and 18-inches away from a cotton fabric target. Samples of gunshot residue were then collected from the fabric target. 5% nitric acid was used to collect the sample and the crystallization was tested by using 3 types of reagents, including Sulfuric Acid, Oxalic Acid, and Potassium Iodide. The test was repeated 5 times for each sample by dropping 10 µL of standard solution on a glass slide and 10 µL of a testing reagent near the standard solution. The crystal formation was observed under a Polarized Light Microscope with 200 magnification power and the crystal shape and color were recorded.

## 4. RESULTS

### 4.1 Sensitivity testing and finding optimum reagent concentration

Three types of standard solutions: $Ba(NO_3)_2$, $Pb(NO_3)_2$ and $Sb(NO_3)_2$ and 3 types of reagent: Sulfuric Acid, Oxalic Acid, and Potassium iodide were used with different concentrations to check for sensitivity to find the optimum concentration of the reaction (reagent) with the microcrystalline technique. The results showed that each standard solution had a different optimum concentration for the reaction with different crystal habits.

#### 4.1.1 Barium (Ba)

When using a standard solution of $Ba(NO_3)_2$ at 100, 200, 300, 400 and 500 mg/L and reacting reagents Oxalic Acid and Potassium Iodide, crystals are not formed. However, when using 5% Sulfuric Acid, the crystal is formed at 300 at 400 mg/L and Barium crystal is isotropic as shown in Fig.1 and Fig.2

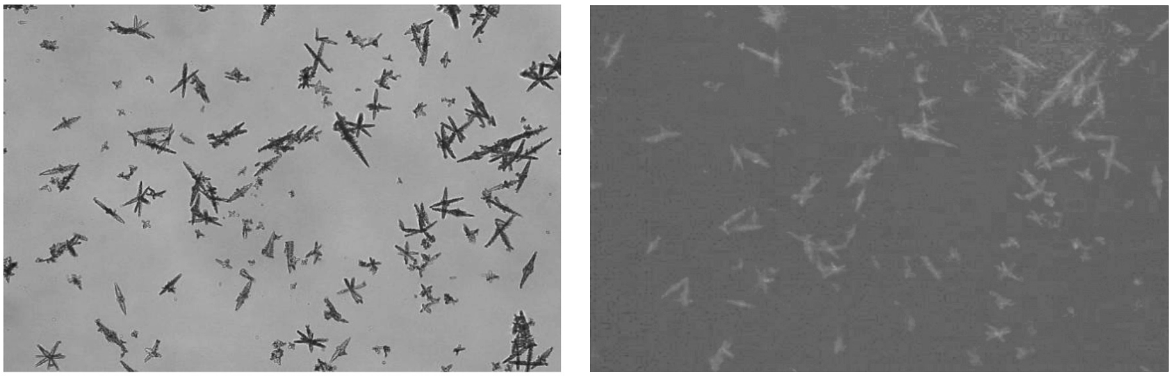

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**Fig. 1** The reaction of $Ba(NO_3)_2$ at 300 mg/L with 5%  Sulfuric Acid at 200X

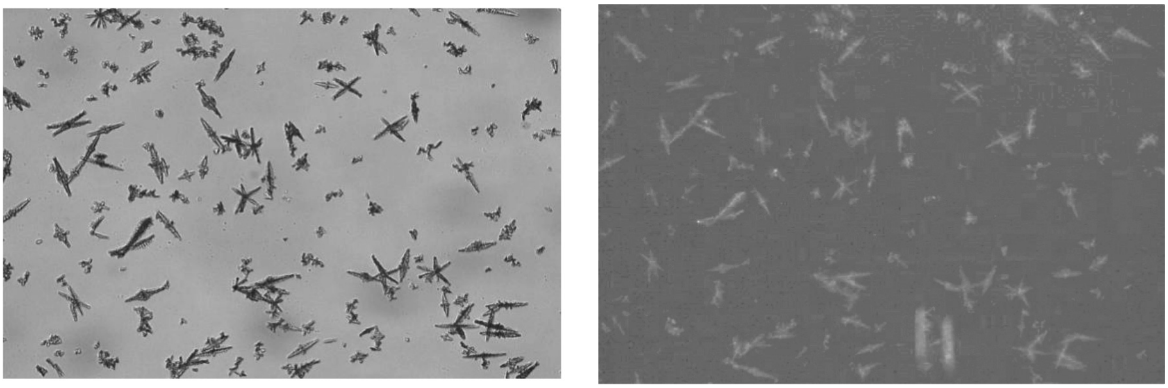

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**Fig. 2** The reaction of $Ba(NO_3)_2$ at 400 mg/L and 5% Sulfuric Acid at 200X

#### 4.1.2 Lead (Pb)

When a standard Pb $(NO_3)_2$ was applied, the concentrations were 100, 200, 300, 400 and 500 mg /L reacted with Oxalic Acid, Potassium Iodide and Sulfuric Acid. The results showed that the crystals were well formed when reacting to the three reagents with optimum concentration.

1) The standard solution concentration of $Pb(NO_3)_2$ was at 200 mg/L. When reacting to 5% Oxalic Acid

2) The standard solution concentration of $Pb(NO_3)_2$ was at 400 mg/L. When reacting to 5% Sulfuric Acid and Potassium Iodide 5% and it was found that the lead crystal was an Anisotropic as shown in Fig 3-5, respectively.

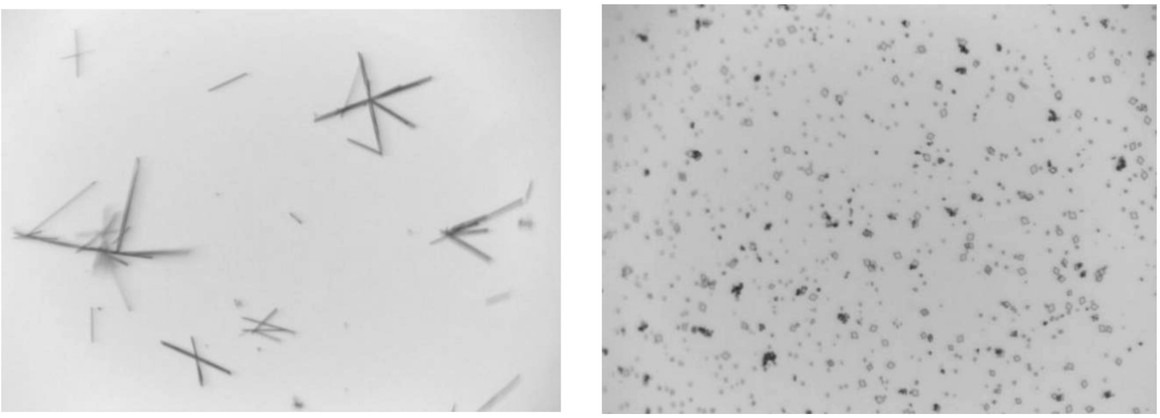

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**Fig. 3** reaction of $Pb(NO_3)_2$ at 200 mg/L and 5% Oxalic Acid

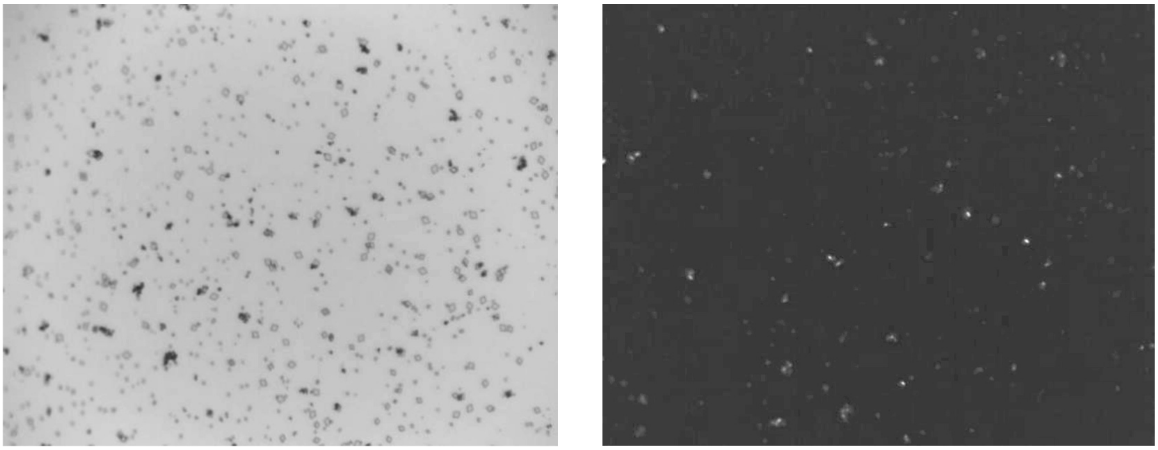

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**Fig. 4** reaction of $Pb(NO_3)_2$ at 400 mg/L and 5% Sulfuric Acid at 200X

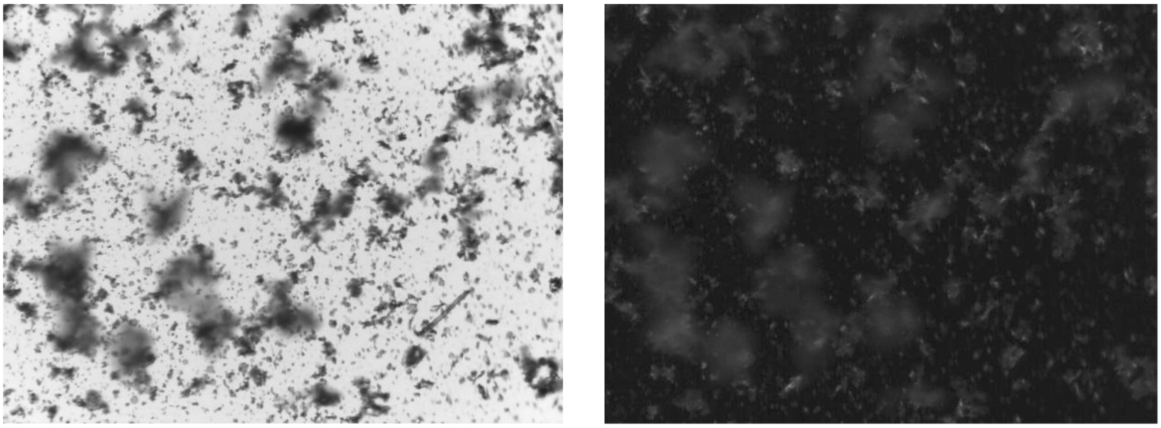

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**Fig. 5** reaction of $Pb(NO_3)_2$ at 400 mg/L and 5% Potassium Iodide at 200X

#### 4.1.3 Antimony (Sb)

When the standard solution of $Sb(NO_3)_2$ was taken with concentrations 100, 200, 300, 400 and 500 mg/L and it reacted to the Potassium Iodide and Sulfuric Acid reagent it was found that no crystals formed, but when using 10% Oxalic Acid crystals formed at concentrations of 300 mg/L. Barium (Ba) crystal is Isotropic, as shown in Fig.6

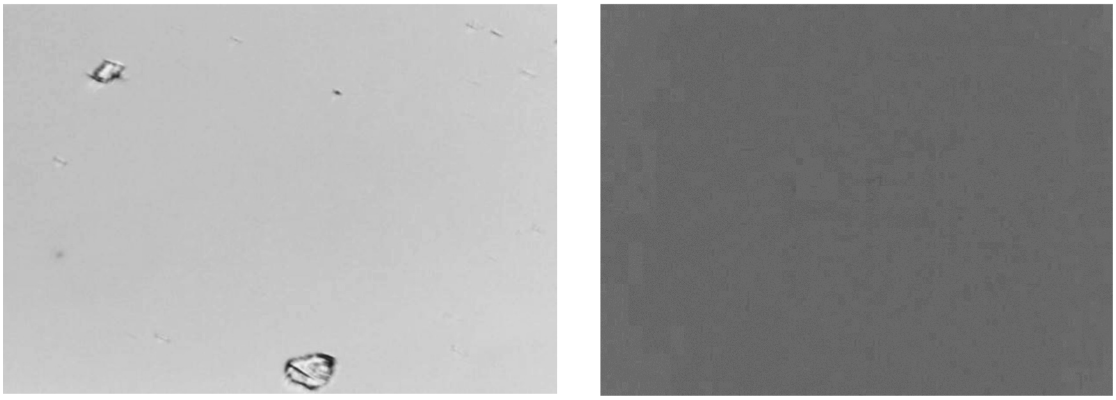

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**Fig. 6** reaction of $Sb(NO_3)_2$ at 300 mg/L with 10% Oxalic Acid at 200X

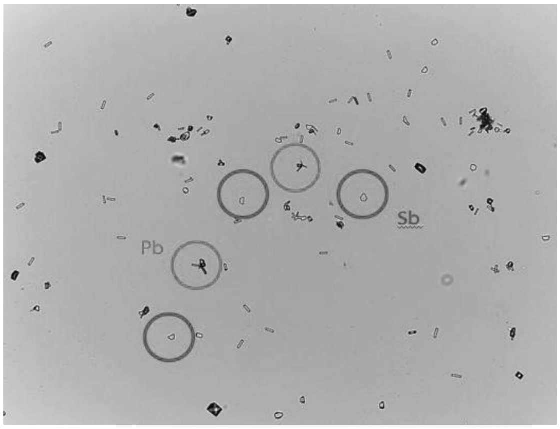
### 4.2. Testing of microcrystalline from gunshot residue

When collecting gunshot residue, two types of Glock guns were used, revolver and semi-automatic pistols. Three shooting ranges were tested: contact, 6-inches, and 18-inches. The testing of microcrystal used 3 types of reagent: 5% Sulfuric Acid (V/V), 10% Oxalic Acid (w/V), and 5% Potassium Iodide (w/V). The results showed that both types of guns had different amounts of soot, resulting in different crystals forming at each distance.

#### 4.2.1 Revolver pistol : the existence of crystal was studied from different shooting ranges as follows:

##### 4.2.1.1 At contact range

Pb and Sb anisotropic crystal are formed when using 10% Oxalic Acid as shown in Fig.7

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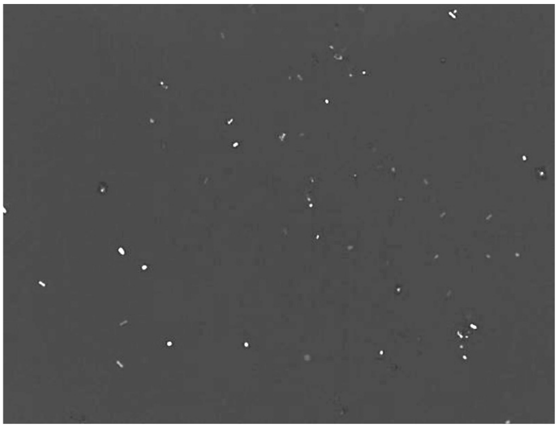

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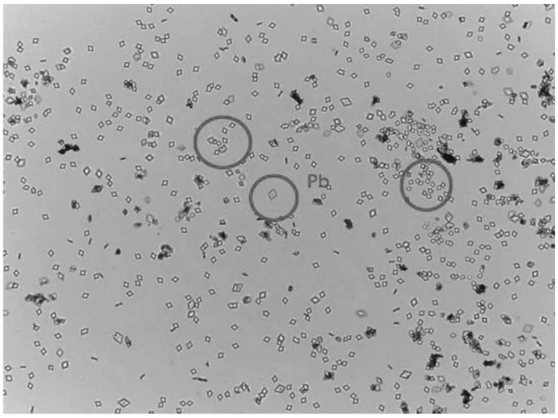
**Fig. 7** reaction of gunshot residue for contact range of revolver with 10% Oxalic Acid at 200X

**4.2.1.2 At six inches range**

At 6 inches shooting range, the lead crystal is formed when using 5% Sulfuric Acid and 5% Potassium Iodide and they are isotropic and anisotropic respectively as shown in Fig.8 and Fig.9

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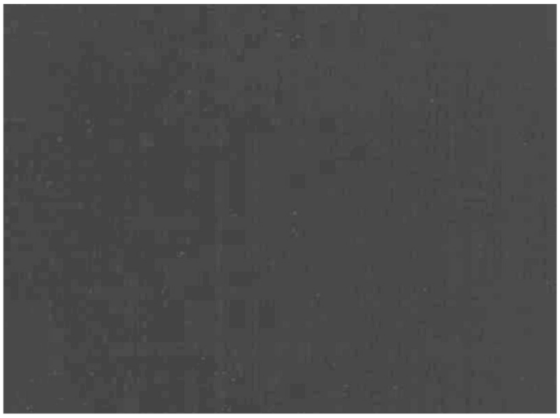

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**Fig. 8** reaction of gunshot residue at 6 inches shooting range with 5% Sulfuric Acid at 200X

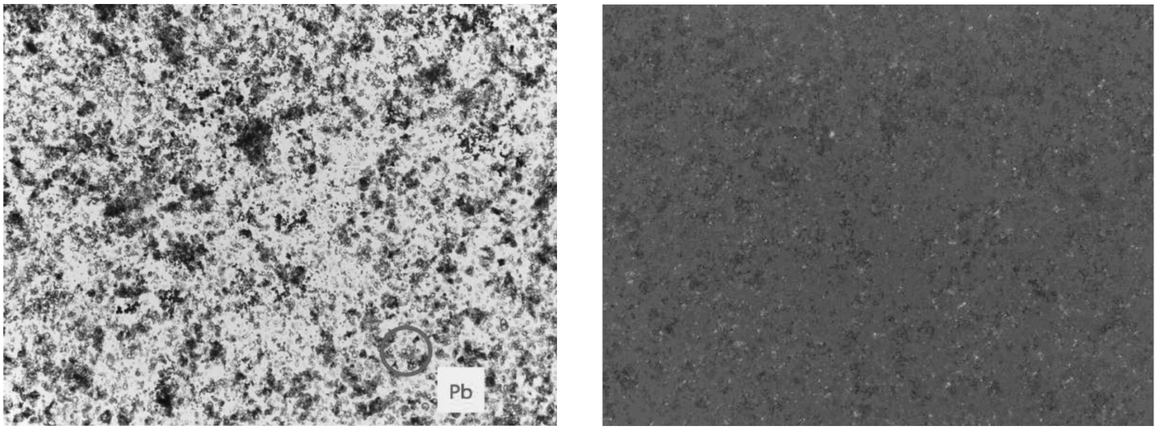


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**Fig. 9** reaction of gunshot residue at 6 inches shooting range with 5% Potassium Iodide at 200X

**4.2.1.3 At 18 inches shooting range**

When testing of crystallization of gunshot residue at 18 inches or more, the results showed that there was very little crystal formation, correlating with the theory of gunshot residue at different ranges.**2.2 GLOCK semi-automatic pistol**

When studying crystals formation of gunshot residue of GLOCK semi-automatic brand, it was found that a complete crystal of the element was well-formed at contact range, but at a distance of 6 inches to 18 inches, there was only a very small amount of crystals consistent with the theory of gunshot residue at different shooting ranges. At contact range, the crystals of Pb were formed when using 5% Sulfuric Acid and it was an isotropic crystal. Anisotropic crystals of Ba were formed when using 5% Potassium Iodide as shown in Fig. 10 and Fig. 11

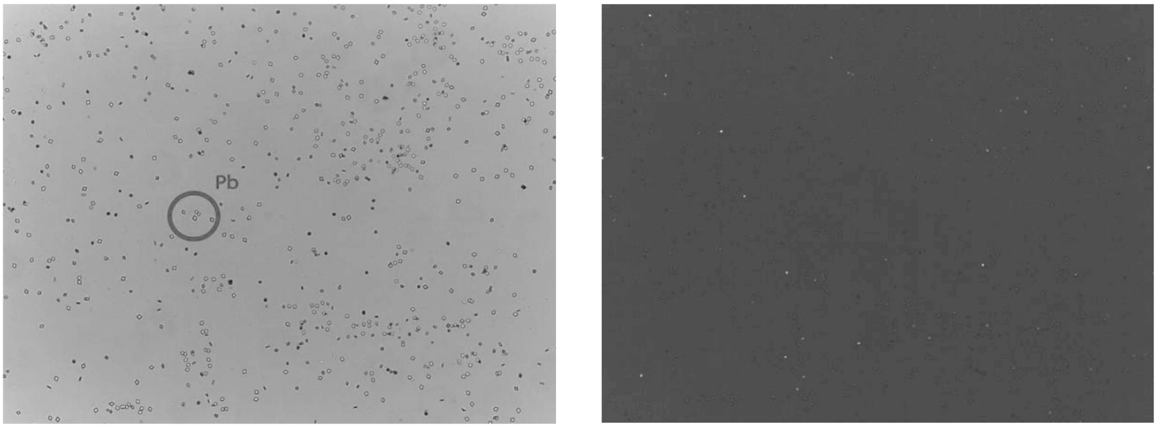


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**Fig. 10** reaction of gunshot residue from GLOCK semi-automatic pistol at contact range with 5% Sulfuric Acid at 200x

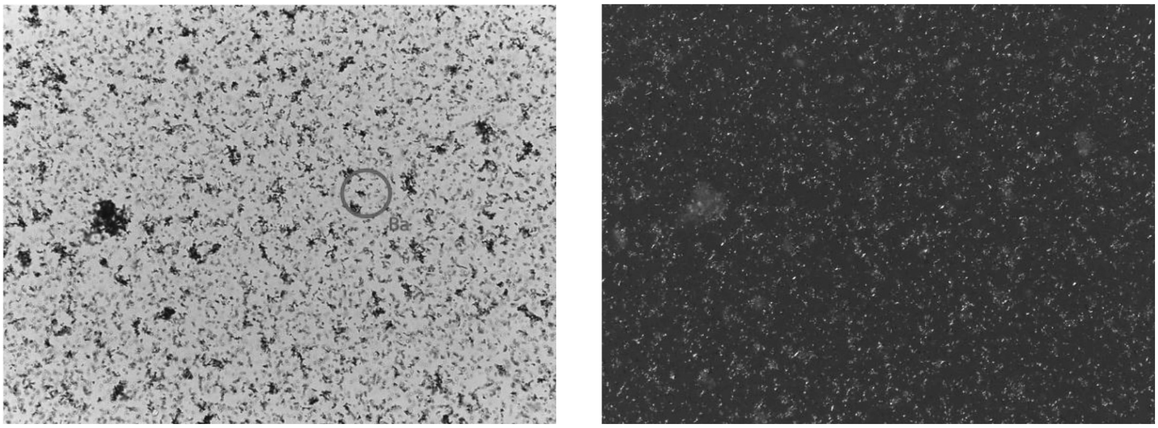


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**Fig. 11** reaction of gunshot residue from GLOCK semi-automatic pistol at contact range with 5% Potassium Iodide at 200x

## 5. CONCLUSION

This research has shown that microcrystalline tests can be effectively used for preliminary analysis of gunshot residue elements. It is a fast and cost-effective technique and it is suitable for detecting the composition of gunshot residue in a laboratory with limited resources.

Gunshot Residues (GSR) analysis technique is an analysis of 3 major components which are Antimony, Barium and Lead. The analysis can be conducted with more complicated and expensive methods such as the Neutron Activation Analysis (NAA), Atomic Absorption Spectrophotometry (AAS), Inductively Coupled Plasma Spectrometry (ICP), and the Scanning Electron Microscope and Energy Dispersive X-ray Spectroscope (SEM/EDX). However, the Microcrystalline technique is less expensive and a relatively fast technique .

This research studied the quantity of reactants for developing microcrystalline in the three main elements of gunshot residue. The best shooting ranges for finding GSR is contact up to less than 6 inches. At 18 inches and over, microcrystals are rarely found. This is an effective preliminary test for gunshot residue and can be applied by remote laboratories with limited resources.

## 6. SUGGESTIONS

6.1 Further studies should collect GSR samples from other types of ammunition and choose other reagents for testing to broaden the examination using the microcrystalline technique.

6.2. The collection of GSR should be done from other sources than clothing to include the hands of the shooter in order to expand the types of the testing samples.

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