

Chemistry and Industry for Teachers in European Schools

FORENSIC CHEMISTRY - CHASE THE CRIMINALS WITH CHEMISTRY

Simple Experiments for Chemistry Lessons

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Translation of parts of the German texts and final English Version by Keith Healey







CITIES (Chemistry and Industry for Teachers in European Schools) is a COMENIUS project that produces educational materials to help teachers to make their chemistry lessons more appealing by seeing the subject in the context of the chemical industry and their daily lives.

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- Czech Chemical Society, Prague, Czech Republic , http://www.csch.cz/
- Jagiellonian University, Kraków, Poland, http://www.chemia.uj.edu.pl/index_en.html
- Hochschule Fresenius, Idstein, Germany, http://www.fh-fresenius.de
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- Newcastle-under-Lyme School, Staffordshire, United Kingdom
- Masaryk Secondary School of Chemistry, Prague, Czech Republic
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MAKING FINGERPRINTS VISIBLE USING POWDERS FOR DETECTION

FUNDAMENTALS

All powders which are mentioned in the following experiment are used in the professional securing of evidence. Universally used agents are iron and iron(III)oxide powders. Ideal surfaces for detecting traces are glass and glazed earthenware. The finger prints made visible can be taken with the aid of a strip of adhesive tape which is then stuck on a piece of white paper and thus fixed permanently.

TIME REQUIRED

15 min

APPARATUS NEEDED

4 fine brushes (eg Milan 8), 4 petri dishes, glass plates/bottles, adhesive tape (if possible a broad adhesive tape), white paper

CHEMICALS

graphite, aluminium bronze, iron powder (fine), iron(III)oxide powder

SAFETY HINTS

aluminium bronze (highly inflammable, F), iron powder (inflammable, F)

PROCEDURE

Fingerprints are left on various materials with a smooth surface. Afterwards small amounts of powders are filled into marked petri dishes and applied either by knocking the brushes over the trace or by directly brushing (gently) over the fingerprint (Caution! Danger of blurring). Excess powder can be blown off.

OBSERVATIONS

The fingerprint becomes visible as a line pattern in the colour of the powder; different powders are suited for surfaces of different materials.

EVALUATION

The powder adheres to the surface because of adhesive forces left by the finger (water, grease, etc.) and thus the powder makes the fingerprint visible by the colour contrasts.

DISPOSAL

Powders left can be further used or disposed of as solid chemical waste.





MAKING FINGERPRINTS VISIBLE USING IODINE

<u>FUNDAMENTALS</u>

Iodine is used as a powder or as vapour, but it may not be used at the site of the crime because of its harmful effects when breathed in (irritation of the mucous membrane) or by contact with the skin. It is especially valuable for paper as the carrier of traces. Because iodine is highly volatile the traces can only be seen for a short time and must be photographed or fixed by a chemical reaction, eg with starch.

TIME REQUIRED

15 min

APPARATUS NEEDED

dropping funnel, rubber pressure bulb, glass wool, rubber stoppers, TLC-chamber, sand bath, heating plate, tweezers, printing paper, cardboard, protective gloves, stand

CHEMICALS

iodine

SAFETY HINTS

iodine (noxious, Xn; hazardous to the environment, N)

PROCEDURE

Fingerprints are left on printing paper or cardboard. All further activities are carried out under the ventilation hood and with gloves.

Alternative 1 (with an "iodine evaporator"): A dropping funnel is first filled with glass wool, followed by iodine and glass wool again. A rubber pressure ball is fitted to the outlet of the dropping funnel. The carrier of the fingerprint traces is vaporised with this "iodine evaporator" (see picture).



When not in use the dropping funnel must be closed with a rubber stopper.





Alternative 2 (with TLC-chamber): Some iodine crystals are spread on the bottom of the TLC-chamber and the carrier of the fingerprint traces is placed in it. The TLC-chamber is closed and and slightly heated on a sand bath.

OBSERVATIONS The fingerprints become visible as a brownish line

pattern.

EVALUATIONIodine sticks to the surface because of the adhesive forces of the substances transferred by the finger

(water, grease, etc.).

<u>Disposal</u> Crystalline iodine is either kept for further use or

disposed of as solid chemical waste.

The traces are only visible for a limited time because iodine is volatile. To fix the traces its carrier should be sprayed with a one-percent starch solution. Before this step excessive iodine should be removed by letting it

stand in the air. The traces become dark blue



MAKING FINGERPRINTS VISIBLE USING CYANOACRYLATE

FUNDAMENTALS

Cyanoacrylate adhesives are one-component adhesives on the basis of monomeric 2-cyanoacrylic-acid esters. They are cured very quickly by traces of water and become high molecular mass, uncross-linked polymers. Fingerprints – especially those on metal and glass – can be made visible as a greyish-white pattern.

As an alternative to the monomer, a cyanoacrylate polymer can be used as the reagent. By its pyrolytic splitting a monomer is obtained which can be polymerised again.

TIME REQUIRED 30 min

APPARATUS NEEDED

crystallisation dish (\emptyset 14 cm), heating plate, rod thermometer, beaker (50 mL), small aluminium dish, aluminium foil, stand material

CHEMICALS

cyanoacrylate (instant adhesive), ethanol, aluminium oxide

SAFETY HINTS

ethanol (inflammable, F), cyanoacrylate (caustic, Xi). Cyanoacrylate agglutinates skin and eyelids within seconds.

PROCEDURE

The metal sheet is degreased with ethanol and some fingerprints are put on it. All additional work is done under a ventilation hood. A vaporisation device is constructed using a crystallisation dish. A 50 mL beaker is half filled with water and placed into the crystallisation dish. A small amount of liquid instant adhesive is applied on the aluminium dish which is afterwards also put in the dish. A rod thermometer is fixed in such a way that half of it is visible in the crystallisation dish. The dish is covered with the aluminium foil and the inner space is heated up to 40-60 °C on the heating plate. The metallic carrier of





traces is suspended on the inner wall of the dish. It can be observed how the fingerprints develop. The process is finished after a few minutes.

OBSERVATIONS

The fingerprints on the piece of metal are visible as a greyish-white line pattern.

EVALUATION

The monomeric cyanoacrylate cures very quickly to give a high molecular mass uncross-linked polymer. This is brought about by traces of water. Because of the relatively high moisture content of the dactyloscopic trace the polymerisation occurs there.

DISPOSAL

The cured cyanoacrylate adhesive is disposed as domestic waste.





SECURING SHOE, FOOT AND VEHICLE TRACES: GYPSUM AS AN AGENT FOR CASTING SHOE PRINTS

FUNDAMENTALS

Beside fingerprints also shoe, foot and vehicle traces constitute valuable hints for clearing up a crime. Such traces are found for example in sand or loose soil. Casting becomes necessary when the originals cannot be saved. Moulding or dental gypsum can be used. To prepare the trace, hair spray or varnish is used as a fixing agent. In the following experiment hairspray and moulding gypsum is used.

TIME REQUIRED

45 min

APPARATUS NEEDED

gypsum bowl, scraper, shallow plastic dish (ca. 50 - 40 cm), wooden or cardboard frame

CHEMICALS

moulding gypsum, hairspray, flower soil

SAFETY HINTS

PROCEDURE

Firstly, a flat plastic dish is filled with a layer of flower soil and a footprint is made. The footprint is fixed with hair spray. As an edging a frame is placed around the footprint. According to the instructions of the supplier the powdery moulding is stirred in water so that a smooth and uniform paste is formed. This paste is carefully poured onto the trace or applied with a scraper. This procedure must be started at the lowest point of the trace. The frame has to be taken away before the gypsum hardens completely, but this edging should only be totally removed after the hardening process is complete.

OBSERVATIONS

The cast provides a three-dimensional mirror image of the original trace.

EVALUATION

The trace (in our case a footprint) is fixed by spraying hairspray on it. The moulding gypsum contains calcium sulfate-hemihydrate. When the gypsum sets, the calcium sulfate – hemihydrate, which is still powdery, reacts with more water to form a solid block of calcium sulfate - dihydrate.

 $CaSO_4 * \frac{1}{2} H_2O + 1 \frac{1}{2} H_2O \rightarrow CaSO_4 * 2 H_2O$

DISPOSAL

Residues of gypsum are disposed of as domestic waste.





HINTS

Before casting a natural impression, the print has to be cleaned of foreign materials such as leaves, wood, stones, etc. Water in the trace is absorbed by paper or removed by a pipette.





REPRODUCTION OF GROUND-DOWN NUMBERS AND LETTERS MAKING TRACES OF EMBOSSINGS ON BRASS DISHES VISIBLE

FUNDAMENTALS

Motor vehicles, firearms and keys of locking systems are typical objects, which are provided with individual codes in the form of letters, numbers or strafing signs, in the case of weapons. If such an object is used in a crime, the offenders frequently remove or change the trace which might betray them. This can be achieved by filing, sanding or drilling away as well as by destroying original signs or engraving of different signs.

Forensic technology uses the method of metallographic etchings, also called structural contrasting, for the reproduction of such cases. The changes within the structure of the material which occurred by the embossing tools during the original imprinting become visible. This will be demonstrated, as an example, by brass dishes and iron(III)chloride as an etching solution. Additional instruction for other etching solutions can be found in the script.

TIME REQUIRED

15-30 min

APPARATUS NEEDED

(non-magnetic) keys made of brass or nickel silver, square file, 'wet and dry' abrasive paper (grain 320, 600, 1000), measuring cylinder (50 mL), petri dishes, crucible tongs (or tweezers), beaker (100 mL), spatula, scales, scoops, paper towels

CHEMICALS

iron(III)chloride (free from water), hydrochloric acid (w/w = 30 %)

SAFETY HINTS

iron(III)chloride (noxious, Xn), hydrochloric acid (corrosive, C)

PROCEDURE

The embossed signs on the keys are removed by a square file so that they can no longer be seen. Afterwards, the surface is polished with abrasive paper (grain 320, 600 and 1000). If wet abrasive paper is used, it must be made properly wet by the addition of a few drops of water.

The etching solution contains 5 g iron(III)chloride in 50 mL hydrochloric acid. The keys are put in petri dishes filled with the etching solution for 10 minutes. If the





results are not satisfactory, this procedure can be repeated up to 5 times. The keys are then washed under running water and dried with paper towels.

OBSERVATIONS

The numbers and letters embossed onto the keys are not visible any longer. After having put them in the acidic iron (III) chloride solution the original marks can be recognised as a grey contrast.

EVALUATION

The embossed numbers and letters become visible because more profound changes in the structure of the material occur during the cold deformation as in the visible numbers and letters. These parts in contact with the oxidizing agent [iron(III) ions] form local elements because brass and nickel silver are alloys containing copper. Because the structure is inhomogenous, potential differences occur which again lead to a differentl degree of wear on the surface.

$$Cu + 2 Fe^{3+} \rightarrow Cu^{2+} + 2 Fe^{2+}$$

DISPOSAL

The acidic heavy metal solutions are neutralised and disposed of as heavy metal waste.

HINTS

To allow a maximised reproduction during a school experiment, it is important not to remove too much of the surface when filing or grinding. Nickel silver consists of approximately 60 % copper, 20 % nickel and 20 % zinc.





INVISIBLE INKS AND FORGERY OF DOCUMENTS PRODUCING BLUE INVISIBLE INK

FUNDAMENTALS Thymolphthalein is an organic dyestuff which can turn

into diferent structures when the pH value changes. In alkaline environment it is blue, in neutral or acidic

environment it is colourless.

TIME REQUIRED 15-30 minutes

<u>APPARATUS NEEDED</u> beakers (100 mL, 2 x 250 mL), measuring cylinder

(100 mL), glass rod, brush, large white filter paper sheets or printing paper, vaporiser, spatula, balance,

scoops

CHEMICALS thymolphthalein, ethanol, sodium carbonate

(anhydrous), sodium hydoxide

SAFETY HINTS ethanol (inflammable, F), sodium carbonate (irritant,

Xi), sodium hydoxide (caustic, C)

PROCEDURE First produce the following solutions:

- 0.04 g sodium hydroxide in 100 mL distilled water,

- 0.04 g thymolphthalein in 50 mL ethanol

- 0.5 g Sodium carbonate in 100 mL water.

Now pour the colourless thymolphthalein solution into the colourless sodium carbonate solution. This mixture of solutions can be used as ink. Write a few words on the filter (or printing) paper with the brush. Spray the leaf with the sodium hydroxide solution after 10

minutes.

OBSERVATIONS The ethanolic thymolphthalein solution is colourless.

When it mixes with colourless sodium carbonate solution, which is also colourless, a blue solution is obtained, which can be used as ink. After approximately 10 minutes the ink applied onto the paper is no longer visible. By spraying with the sodium

hydroxide solution the message becomes visible again.

EVALUATION When dissolving sodium carbonate in water, hydroxide ions are produced - the solution becomes alkaline.

 $Na_2CO_3 + H_2O \rightarrow 2Na^+ + HCO_3^- + OH^-$





The indicator thymolphthalein, which is added, causes the solution to become blue. With this blue ink a message can be written. When the dyestuff solution is exposed to air, the originally alkaline solution is neutralised by the carbon dioxide in the atmosphere (which contains 0.03% (by volume) carbon dioxide. The structure of the dyestuff is also changed as its pH changes from an alkaline to a neutral value. The ink becomes colourless. The message cannot be read any longer. When the ink is sprayed with sodium hydroxide solution again, an alkaline environment is obtained once more and consequently the indicator changes back to blue. The two structures in which thymolphthalein can exist.

thymolphthalein

DISPOSAL

The remaining solutions can be disposed of down the drains.





INVISIBLE INKS AND FORGERY OF DOCUMENTS PRODUCING INK WHICH IS VISIBLE FOR A SHORT TIME

<u>FUNDAMENTALS</u>

An ink visible for a short time can be easily produced with starch. When the ink dries, the message "disappears". For this purpose only **starch-free** filter paper can be used as the carrier. Ordinary printing paper does contain starch. When the invisible ink is sprayed with an iodine/potassium iodide solution, The message "returns". Reacting with sodium thiosulfate the message becomes invisible again.

TIME REQUIRED

30 minutes

APPARATUS NEEDED

beakers (100 mL, 3 x 250 mL), measuring cylinder (100 mL), magnetic heating plate (with magnetic stirring bar), sheets of filter paper, two vaporisers, brush, spatula, glass rods, balance, scoops

CHEMICALS

iodine, potassium (or sodium) iodide, starch, sodium thiosulfate-pentahydrate, ice

SAFETY HINTS

iodine (noxious, Xn; environmentally hazardous, N)

PROCCEDURE

First prepare the invisible ink. For this purpose suspend 1 g soluble starch in 100 mL distilled water. Add approximately 50 mL boiling distilled water and keep it boiling gently for the next 5 minutes. Then add 40 mL iced water.

Write a secret message on filter paper and let the ink dry.

To make the message visible again a solution of iodine is needed. This solution consists of 1.70 g potassium iodide and 2.50 g iodine, which are dissolved in 100 mL distilled water. Pour the solution in a vaporiser and spray the message with this iodine/potassium-iodide solution. (If *sodium* iodide is used, 1.54g is required.)

The message which has appeared can be made to disappear again by spraying it with the following solution. Dissolve 2.32 g sodium thiosulfate-pentahydrate in 50 mL distilled water and make it up to 100 mL after dissolving.



OBSERVATIONS

Originally the ink is faintly visible and after drying the starch suspension has become completely invisible. By spraying it with an iodine/potassium iodide solution, the writing takes on a bluish colour. The treatment with a sodium thiosulfate pentahydrate solution allows it to make the message disappear again.

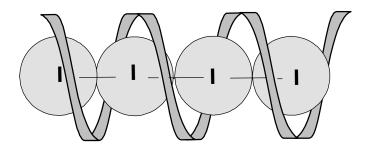
EVALUATION

Iodine is hardly soluble in water at room temperature. The solubility of iodine in water is considerably increased by adding KI. I_2 molecules form I_3^- ions together with iodide ions, which are very soluble in water.

$$I_2 + KI \rightarrow KI_3$$

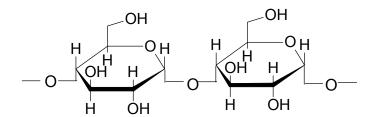
(or
$$l_2 + l^- \rightarrow l_3^-$$
)

Iodine forms a violet-blue complex with the amylose contained in starch. The iodine molecules insert themselves into the convolutions of the amylose, this being the reason why the violet colour occurs.



Iodine-molecule in a twisted amylose molecule

Amylose is a long-chain molecule consisting of glucose molecules, which are linked in an a(1,4)-glycosidical way, the reason why the convolutions of the amylose molecules come into existence.



Two linked glucose molecules from an amylose molecule





Iodine and potassium iodide form a dark red-brown solution when dissolved together in water. When iodine reaches those parts of the filter paper where starch can be found, both substances form the violet-blue complex described above and the writing becomes visible through the starch solution.

 I_2 molecules, that is to say elementary iodine, are necessary so that the iodine-starch complex can be formed. The elementary iodine is reduced to iodide ions (I^-) in the complex by sodium thiosulfate. Iodide ions by themselves cannot form the violet-blue iodine-starch complex; the complex is destroyed and the writing becomes colourless again. The thiosulfate ion ($S_2O_3^{2-}$) is oxidised to tetrathionate ($S_4O_6^{2-}$).

DISPOSAL

The starch solution can be disposed of in waste water. Add the remaining iodine/potassium iodide solution with the sodium thiosulfate solution and dispose of it with the liquid heavy metal waste





INVISIBLE INKS AND FORGERY OF DOCUMENTS INVISIBLE PEN

FUNDAMENTALS The "Invisible Pen" ™ is a commercially available writing

utensil filled with an "invisible" ink. The written messages can only be seen with the help of a very

small UV lamp which is part of the set.

TIME REQUIRED 1 minute

APPARATUS NEEDED Invisble Pen, edding 8280 Securitas UV-Marker, UV-

lamp, printing paper

CHEMICALS -

SAFETY HINTS -

PROCEDURE Write something on a piece of paper with the "Invisible

Pen" or with the "edding 8280 Securitas UV-Marker".

Illuminate the message with the UV lamp afterwards.

OBSERVATIONS The written message is initially invisible. In the UV light

it appears as a faint blue/violet writing.

EVALUATION The "Invisible Pen" contains a dyestuff which is not

defined in detail, but which does not absorb visible light and so does not show a colour. However, it is excited by UV light and emits light in the violet-blue spectral region (luminescence). Luminescence occurs when an electron falls from an energetically higher to an

energetically lower, unoccupied state.

HINTS The "Invisible Pen" including the UV lamp can be

obtained for approx. €5 from Pearl-Versand, a dispatching company, www.pearl.de. The "edding 8280 Securitas UV-Marker" can be obtained from paper

shops.





BLOOD HAEMOGLOBIN TEST (TEICHMANN-TEST, ALTERNATIVE 1)

FUNDAMENTALS

Haemoglobin is the pigment of the red blood cell. It consists of the colour component haem and the protein component globin. Both are combined in the form of a complex. One haemoglobin molecule contains four haems.

One haem group consists of a modified porphyrin ring together with a bonded iron(II) ion. This is responsible for the transport of oxygen in blood.

For every iron atom, one molecule of oxygen is bonded without any change in the level of its oxidation state.

The haem can easily be transformed to haematin, in which iron exists as the iron(III) ion.

The following Teichmann test also works with blood that is several centuries old. Two alternatives are explained here:

TIME REQUIRED

30 minutes

APPARATUS NEEDED

Microscope (magnification 500-fold), mortar and pestle, burner, dropping pipette, microscope slide, slide cover glasses, spatula, test tube clamp

CHEMICALS

sodium chloride, concentrated acetic acid, pig's blood

SAFETY HINTS

acetic acid (corrosive, C)

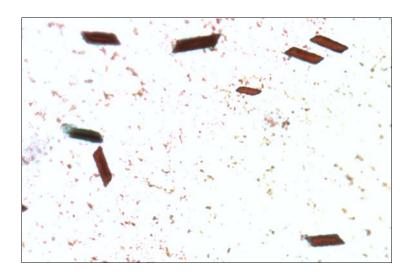




PROCEDURE

A drop of blood is put on a microscope slide, then spread out evenly with a second microscope slide and dried for 5 to 10 minutes. At the same time a little (!) NaCl is ground in the mortar. The blood is scraped off with the microscopic slide and put on another one which is clean. A trace of the NaCl is mixed with it. Two drops of concentrated acetic acid are put on it and covered with a slide cover-glass. Afterwards the microscopic slide (can crack) is held into the bright flame with a clamp and heated to boiling.

After the microscope slide has cooled down, the sample can be investigated under the microscope. One should begin with the smallest magnification and slowly move the microscope stage to obtain a sharp image. In some cases it might be necessary to repeat this with a larger lens. The crystals must be clearly visible (see picture).



(from: Ifbz Chemie Frankfurt/M.; 160-fold magnification with a light microscope)

OBSERVATIONS

Many huge crystals can be recognised under the microscope. These are NaCl crystals which were not dissolved and did not react. Only at the next level of magnification many fine, needle shaped crystals can be recognised between them. They are dark brown.

EVALUATION

Teichmann's crystals are those, in which the chloride of the haematin – the haemin – is present. (see structure above).

DISPOSAL

The microscope slides are disposed of in domestic waste.





<u>Hints</u>

During heating a delay in boiling may quickly occur because of the viscosity of the blood (wear goggles).

- The microscope slide is not suited to high temperatures and can crack at high temperatures (wear goggles).
- The experiment can be carried out without a slide cover-glass or with a second microscope slide instead.
- Too much NaCl masks the haemin crystals.
- The microscope slides can become sooty.





BLOOD HAEMOGLOBIN TEST (TEICHMANN-TEST, ALTERNATIVE 2)

TIME REQUIRED 20 min

<u>APPARATUS NEEDED</u> as in alternative 1, additionally a measuring cylinder

(10 mL), test tube

CHEMICALS as alternative 1

SAFETY HINTS acetic acid (corrosive, C)

PROCEDURE 2 mL blood are put in a test tube with a trace of the

pulverised NaCl as well as 3 to 4 drops of concentrated acetic acid added and mixed. The solution is carefully brought to the boil over the burner, using its blue flame and reduced to approximately 2/3 of its original

amount.

After cooling, place a drop on a microscope slide and spread it. When the drop is dry (if necessary heat it under the luminescent flame) it can be put under the

microscope.

You should begin with the smallest magnification and slowly move up the microscope stage until the sample is well focused. In some cases it might be necessary to repeat this with a larger lens. The crystals must be

clearly visible (see picture above, alternative 1).

OBSERVATIONS In this case additional NaCl crystals are visible, but

clearly fewer than in alternative 1. Among these crystals rhombic brown crystals, whose surface appears partly bluish, can be recognised. The haemin crystals are less numerous but distinctly larger and

consequently easier to recognise.

EVALUATION Teichmann's crystals are those, in which the chloride of

the haematin – the haemin – is present. (see structure

above, alternative 1).

DISPOSAL the microscope slides are disposed of in domestic

waste.

HINTS see alternative 1





BLOOD DETECTING TRACES OF BLOOD WITH LUMINOL

FUNDAMENTALS

The safe and characteristic detection method with an aqueous luminol solution makes even tiny traces of blood visible which cannot be noticed by the naked eye. Luminol shows a strong chemiluminescence together with hydrogen peroxide. To put it simply, visible light is emitted during a chemical reaction because chemical energy is changed into electronic energy which is then released (from: www.experimentalchemie.de)

TIME REQUIRED

30 minutes

APPARATUS NEEDED

Beaker (100 mL, 250 mL), rinsing bottle, two strips of cotton, measuring cylinder (10 mL), spatula, laboratory ballance, disposable pipettes, disposable gloves

CHEMICALS

luminol (5-amino-2,3-dihydrophthalazin-1,4-dion), so-dium carbonate, hydrogen peroxide (w = 30 %), pig's blood, ketchup

SAFETY HINTS

hydrogen peroxide (caustic, C), sodium carbonate (irritant, X_i)

PROCEDURE

Put a few drops of pig's blood on one strip of cotton, on a second put some ketchup. Then prepare a luminol solution in a 250 mL beaker as follows:

0.1 g luminol and 5 g sodium carbonate are dissolved in 100 mL demineralised water and 15 mL hydrogen peroxide are added. Decant this luminol solution into a rinsing bottle (so that undissolved parts remain in the beaker) and spray this solution onto the strips contaminated with blood and ketchup in a dark room. Observe what happens and repeat the procedure, if necessary.

OBSERVATIONS

After spraying the blooded cotton strip with the luminol solution, it appears to glow for a moment. The procedure can be repeated several times. The cotton strip with the ketchup will not show any reaction.

EVALUATION

Luminol is oxidised to diazachinon in alkaline solution under the action of hydrogen peroxide. In the course of the reaction an oxidation to peroxodianion. The nitrogen molecules are split off because of the catalytic effect of the protoferro haem in the blood and then the





aminophthalic acid dianion is formed in an excited state. By emitting light energy the ground state is reached again.

Reaction of the luminol solution with blood (in the presence of hydrogen peroxide) catalyst: haem





Haem (in a narrow sense: protoferro haem - iron(II) complex of the protoporphyrins)

DISPOSAL

the remaining luminol solution is neutralised with diluted hydrochloric acid and disposed of into the drains system.



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