

Classical qualitative analysis. 2. Spot test analysis

Only some drops of investigated solution and reagent are required to make spot test analysis. The analysis is based on "analysis of spots" when bright stains are created as a result of reaction performed on a blotting-paper. During the process products of adsorption of colorful compounds and automatic draining of sediments are accumulated in the centre of the spot. The method is very efficient that is why even minimal amount of product is detectable with naked eye (whereas the same amount of products reaction carried out in a test tubes is difficult to perceive).

Filter paper is recommended for the droplet reaction. Its fibrous structure contains big number of capillaries that increases the surface area. A solute adsorbs effectively on the surface whereas a solvent spreads concentrically due to capillary action. As a result of adsorption on the fibres surface the concentration of reactants increases as well as the sensitivity and rate of reaction. There are some additional advantages of using the blotting paper. Owing to capillary action and selective adsorption the separation of ions is possible especially ions that can inhibit or mask a particular reaction. The selective adsorption is related with a speed of diffusion through capillary fibres, which is different for particular ions. Within the drop of solution placed on the blotting paper there are translocation and segregation of ions into concentric zones. Each ion of particular zone can be recognized by identification tests.

Technique of droplet reaction on blotting paper:

1. There should be enough solution within a capillary to prevent a droplet from hanging down (dip the capillary into an analyzed solution at the depth of 1-2 mm, let the liquid goes up freely until it itself stops)
2. The droplet should not fall down on the paper. A spot is created when the end of capillary touches the surface of the paper as a result of unimpeded outflow.
3. The surface area of the spot should not be too big. In case of a large size of primary stains, the blotting paper stop absorbing the liquid, that can leak laterally without reacting with the solution. Such situation leads to a waste of reagents and results of reaction are ambiguous. The final size of the stain depends on the size of primary spot. To limit the size of the spot, the capillary should not touch the paper for too long; when the size reaches 2-3 mm the capillary has to be removed immediately.
4. One should make effort to produce the oval primary stain, it makes the reagent to cover the spot evenly and provides more accurate results. During application of the reagents the capillary should be positioned in the centre of the existing spot, the paper can be supported underside with index finger nearby the spot. Press the paper with the capillary until the reagent wet the whole spot, then remove the capillary.
5. While the capillary is touching the primary spot of analyzed solution, a part of the solution is absorbed by the capillary with the reagent. When the capillary is dug in the reagent many times these make the reagent more and more contaminated with the investigated solution and as the consequence unusable. In order to prevent the contamination every time the capillary is removed from the wet spot, the wet end of the capillary should be put against the clear blotting paper. Leaking droplet of solution rinses the end of capillary and make it ready to reuse.

Precipitation, filtration and rinsing of sediments on the blotting paper

If the solution contains only one cation many reagents can cause formation of distinct stains on the blotting paper, whereas the presence of other cations can diminish sensitivity of detection and sometimes makes detection impossible. There are some factors that can effect detection:

1. Cations present in the solution react with the reagent and produce spots of identical color as an examined cation does. e.g. Pb^{2+} ions and Na_2S produce black spot of PbS on the paper. Ions: Co^{2+} , Ni^{2+} , Bi^{3+} , Cu^{2+} and others reacting with Na_2S form black spots of adequate sulphides. Evidently in such cases detection of Pb^{2+} in form of PbS is inconceivable.
2. Cations present in the solution react with the reagent and produce spots which color differs from the color an examined cation but the final color of spot is altered.
3. Although cations present in the solution do not create colorful spots with the reagent but because of their natural color, to some extent, they can alter and disturb detection of the ion. The degree of disturbances depends on the concentration of the cations. When the reagent is used in alkaline environment the concentration of colored hydroxides can be too high to detect the examined ion.

In all mentioned cases it is recommended to precipitate the examined ion on the blotting paper and then to rinse out other ions. Unknown ion, gathered on relatively small area of the paper, together with the

appropriate reagent create characteristic colorful spot. E.g. detection of Pb^{2+} ion in form of PbS in the presence of other cations.

Experimental procedure

Detection of Pb^{2+} ion. Put a drop diluted 2n H_2SO_4 on the blotting paper, wait till the whole liquid sinks into the paper. Add a drop of analyzed solution in the centre of the wet spot and then put another drop of H_2SO_4 . As a consequence there is PbSO_4 precipitated on the paper and the other cations (that can disturb Pb^{2+} detection) are filtered into a surrounding sediment blotting paper layers. In order to remove definitively the disturbing cations from PbSO_4 sediment, touch the sediment with capillary containing H_2SO_4 solution several times. Sulphuric acid is added as long as a diameter of the wet spot is doubled. Next, excess of H_2SO_4 is rinsed from the sediment with water.

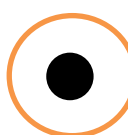
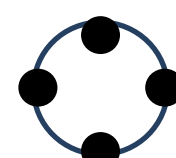
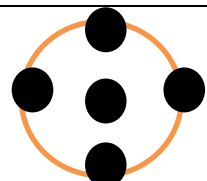
Technique how to rinse the sediment is as follows. Take the water as much as possible to a capillary, try the water not to leak from the end. Touch the centre of the sediment spot with the end of capillary and press on the paper carefully. While the water is flowing out the capillary it rinses evenly the whole sediment and takes removed admixtures towards a periphery of the spot. During this process the size of the wet spot is increasing. Only water should be present within the narrow zone that surrounds the sediment directly. After the whole wet spot is moistened with Na_2S solution there is a black spot of PbS in the centre; the black spot is surrounded by colorless zone, next black or dark brown ring containing sulphides of other cations. The presence of colorless zone is a proof of well performed rinsing, lack of the zone or when the black spot is edged directly with the peripheral brown ring these throw doubt on the process of removal of other cations from the sediment and question if the black spot in the centre is caused only by PbS , not by sulphides of other metals.

To guarantee correctness of the procedure, there is no need to moisten the whole wet spot with Na_2S , it is enough to draw up the capillary with Na_2S through the centre of the spot. As a results there will be three dark spots: two outermost in the peripheral ring and the third – central, containing PbS . Obviously in case of lack of Pb^{2+} ion the central black spot will not be created; the colorless wet centre will be surrounded by brown or black ring of other sulphides. When Pb^{2+} is mixed with other ions the formula that represents the detection can be present as follows (u.s. = unknown solution): $\text{H}_2\text{SO}_4 + \text{u.s.} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{Na}_2\text{S}$.

It is absolutely essential to be skilled at obtaining accurate results by practicing precipitation, filtration and rinsing PbSO_4 on the blotting paper and application of Na_2S solution. It is recommended to prepare three unknown solutions (u.s.) of the following compositions: 1. Pb^{2+} , 2. Co^{2+} , 3. $\text{Pb}^{2+} + \text{Co}^{2+}$.

During detection of Pb^{2+} cation it is necessary to follow the instruction applied to the ion and use as unknown solutions the following combinations. One should produce 3 spots.


Detection of Pb^{2+} ion in the presence of Co^{2+} ion; $K_{\text{SO}}(\text{PbSO}_4) = 2 \cdot 10^{-8} > 1 \cdot 10^{-29} = K_{\text{SO}}(\text{PbS})$:

Reactions	Scheme of spots	Photos of spots
1) $\text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \downarrow$ white $\text{PbSO}_4 \downarrow + \text{S}^{2-} \rightarrow \text{PbS} \downarrow + \text{SO}_4^{2-}$ black sediment in the centre of the spot		
2) $\text{Co}^{2+} + \text{SO}_4^{2-} \rightarrow \text{Co}^{2+} + \text{SO}_4^{2-}$ $\text{Co}^{2+} + \text{SO}_4^{2-} + \text{S}^{2-} \rightarrow \text{CoS} \downarrow + \text{SO}_4^{2-}$ black sediment at the margin of the spot		
3) $\text{Pb}^{2+} + \text{Co}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \downarrow + \text{Co}^{2+}$ $\text{PbSO}_4 \downarrow + \text{Co}^{2+} + 2\text{S}^{2-} \rightarrow \text{PbS} \downarrow + \text{CoS} \downarrow + \text{SO}_4^{2-}$		

Detection of Co²⁺ Ion. When a drop of Co²⁺ is applied on the blotting paper and next a drop of KSCN is added a blue color spot is observed as a result of unstable complex salt formation: $\text{Co}^{2+} + 4\text{SCN}^- \rightarrow [\text{Co}(\text{SCN})_4]^{2-}$. When the salt is treated with water the salt dissolves and the color disappears. Inversely while the spot is being dried over the flame of burner the color of stain is enhanced and reaches the maximum. The reaction is very sensitive and make detection of Co²⁺ possible even in the presence of all other cations. In case when big amount of Fe³⁺ ions is present during drying of the paper a green spot can be created. Addition of water causes rinsing of $[\text{Co}(\text{SCN})_4]^{2-}$ from Fe(OH)₃ and as the blotting paper is drying a blue ring around the yellow/red-brown spot is being formed. During detection of Co²⁺ follow the procedure: KSCN + u.s. + KSCN + NH₃(vapor) + H₂O + heating
NH₃ precipitates Fe(OH)₃; Ni(NH₃)₆²⁺ produces light blue tint.

Test solutions: 1. Co²⁺, 2. Ni²⁺, 3. Fe³⁺, 4. Fe³⁺ + Co²⁺.

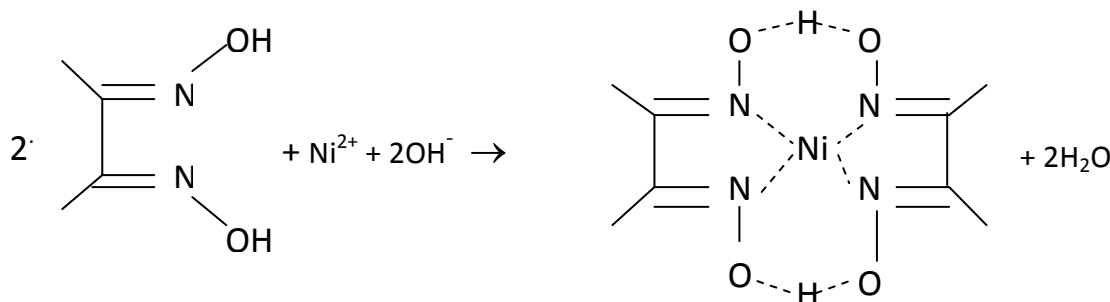
Detection of Co²⁺ ion in the presence of Fe³⁺ ion (equations of 2 stages of reaction):

<p>1) $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \cdot \text{H}_2\text{O} \leftrightarrow [\text{Co}(\text{NH}_3)_6]^{2+} + 12\text{H}_2\text{O}$ $\text{Fe}^{3+} + 3\text{NH}_3 \cdot \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_3 \downarrow + 3\text{NH}_4^+$ dark brown sediment in the center of the spot</p> <p>2) $[\text{Co}(\text{NH}_3)_6]^{2+} + 4\text{SCN}^- \leftrightarrow [\text{Co}(\text{SCN})_4]^{2-} + 6\text{NH}_3 \uparrow$ blue ring around the spot</p>		
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Detection of Ni²⁺ ion

Reaction with dimethylglyoxime is the most sensitive, specific and standard reaction for Ni²⁺ ions. When a drop of salt of Ni²⁺ solution is applied on the paper and then a drop of dimethylglyoxime solution is added, a red or pink spot is formed. The intensity of color can be enhanced when it is treated with ammonia vapor. During detection of small amount of Ni²⁺ it is necessary to use NH₃, that strengthens the sensitivity of reaction with dimethylglyoxime. However in such a case, naturally in the presence of big amount of Fe³⁺ and Cu²⁺ detection of Ni²⁺ by means of dimethylglyoxime is impossible. Fe³⁺ under influence of NH₃ forms Fe(OH)₃ – yellow/ red-brown spot; Cu²⁺ with dimethylglyoxime create pink-brown tint, during reaction with NH₃ solution – complex cation is stained with intensive blue color. If the reaction is carried out on the blotting paper logged with sodium orthophosphate hydrate, ferric and cupric orthophosphates are produced that cannot be altered by NH₃ and dimethylglyoxime solutions. Pink tint is observed at the margin of the spot after water addition, this color indicates the presence of nickel.

Scheme: Na₃PO₄ + u.s. + Na₃PO₄ + dimethylglyoxime + NH₃ (vapor) + H₂O



Perform 5 spots:

1. Ni²⁺ + dimethylglyoxime + NH₃ (vapor),
2. Fe³⁺ + dimethylglyoxime + NH₃ (vapor),
3. Na₂HPO₄ + Ni²⁺ + dimethylglyoxime + NH₃ (vapor),
4. Na₂HPO₄ + Fe³⁺ + dimethylglyoxime + NH₃ (vapor),
5. Na₂HPO₄ + (Fe³⁺ + Ni²⁺) + dimethylglyoxime + NH₃ (vapor).

Detection of Al^{3+} ion. Some ions reacting with alizarin create colorful connections called "lacquer". Aluminum lacquer is stained with red color that makes it useful for Al^{3+} ion detection. Put a drop of Al^{3+} on a the blogging paper next treat it with NH_3 vapor, as a result $\text{Al}(\text{OH})_3$ is created. Afterwards moisten the spot with alizarin solution and reuse NH_3 . As a consequence of the reaction between $\text{Al}(\text{OH})_3$ and alizarin, there is a red-pink stain of aluminum lacquer against the violet. In alkaline environment alizarin turns to violet. During heating ammonia escapes and makes violet tint to disappear. Finally only pink stain is observed. When the spot is treated once more with alizarin solution, NH_3 vapor and heating, the tint is enhanced. When there is a trace amount of Al^{3+} , in order to avoid false conclusion concerning absence of Al^{3+} in the unknown solution, the mentioned procedure should be repeated three times.

When aluminum is mixed with other ions it can be detected by following course of actions:

$\text{K}_4[\text{Fe}(\text{CN})_6] + \text{u.s.} + \text{H}_2\text{O} + \text{NH}_3(\text{vapor}) + \{\text{alizarin} + \text{NH}_3(\text{vapor}) + \text{heating}\}$ (repeat three times)

$\text{Al}_4[\text{Fe}(\text{CN})_6]_3$ is soluble in H_2O , whereas cations of other elements reacting with $\text{K}_4[\text{Fe}(\text{CN})_6]$ create insoluble sediments of (Fe^{3+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Ca^{2+}). Around the colorful spot there is a watery zone where Al^{3+} ion migrates. The wider zone the more effectively aluminum is detected.

Sometimes results suggest the absolute lack of Al^{3+} whereas the big amount of it is present in the solution. It may happen when a big amount of acids are present in the solution and when NH_3 treatment was insufficient then the zone surrounding the spot after alizarin application stays colorless. Therefore during NH_3 treatment it is recommended to totally neutralize the acid and form $\text{Al}(\text{OH})_3$.

One should carefully execute detection of Al^{3+} in the presence of big amount Cu^{2+} , since in this case a pink ring can be also produced. When the amount of $\text{K}_4[\text{Fe}(\text{CN})_6]$ is inadequate not all cuprum ions are precipitated in the centre of the spot but some of them migrate towards the margin. In such case the following procedure is required:

$\text{K}_4[\text{Fe}(\text{CN})_6] + \text{u.s.} + \text{Na}_2\text{S} + \text{HCl} + \text{NH}_3(\text{vapor}) + \text{alizarin} + \text{NH}_3(\text{vapor}) + \text{heating}$.

Then CuS (insoluble in hydrochloric acid) stays in the centre of the spot in form black sediment whereas AlCl_3 solution migrates towards periphery.

Perform 5 spots:

1. $\text{Al}^{3+} + \text{NH}_3(\text{vapor}) + \text{alizarin} + \text{heating}$,
2. $\text{Fe}^{3+} + \text{NH}_3(\text{vapor}) + \text{alizarin} + \text{heating}$,
3. $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{Al}^{3+} + \text{H}_2\text{O} + \text{NH}_3(\text{vapor}) + \text{alizarin} + \text{heating}$,
4. $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{Fe}^{3+} + \text{H}_2\text{O} + \text{NH}_3(\text{vapor}) + \text{alizarin} + \text{heating}$,
5. $\text{K}_4[\text{Fe}(\text{CN})_6] + (\text{Al}^{3+} + \text{Fe}^{3+}) + \text{H}_2\text{O} + \text{NH}_3(\text{vapor}) + \text{alizarin} + \text{heating}$.

Analysis of an unknown mixture of ions

Each student receives a test tube with 5 drops of solutions. They are obligated to identify 2 of 4 metallic ions by means of spot test analysis. The method of analysis should be described with the appropriate reaction equations.