Detection of anions

Detection of anions

- no system similar to that for cations
- detection reactions are sufficiently selective
- reactions:
  - Neutral solution × acid medium ⇒ evolution of gases: CO_3^{2-}, SO_3^{2-}, S^{2-}, HS^-, NO_3^-, NO_2^-
  - Removing of HM:
    - boiling with 1M Na_2CO_3 ⇒ insoluble carbonates, however, uwanted losses and changes occure :
      - oxidation SO_3^{2-}, S^{2-}, NO_2^-
      - adsorption on precipitates of carbonates: SO_4^{2-}, PO_4^{2-}
      - loss of volatile acids after acidification with HNO_3
    - using ion-exchangers– exchange for Na^+
    - boiling with MgO: can not be used for detection of PO_4^{2-}, AsO_4^{2-}, CO_3^{2-}

Group reactions of anions

A. precipitation: Ba^{2+}, Ag^{+} ; solubility = f(conditions)

- I. precipitation reactions of Ba^{2+}
  - Ba salts insoluble in strongly acid medium

    2M HCl, 2M HNO_3 : SO_4^{2-}
  - Ba salts insoluble in weakly acid medium

    2M HAc : F^-, CrO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$
  - Ba soli insoluble in neutral medium (water)

    PO_4^{3-} , AsO_4^{3-}, CO_3^{2-}, BO_2^-

Group reactions of anions

- II. Precipitation reactions of Ag^+ (in neutral medium)
  - Ag salts <u>insoluble in 2M HNO_3</u>
    Cl^-, Br^-, I^-, SCN^-, CN^-, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, S^{2-}
  - Ag salts <u>stable only in neutral medium, soluble in HNO_3</u>
    CrO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, PO_4^{3-}, AsO_3^{3-}, AsO_4^{3-}, CO_3^{2-}, BO_2^-
  - Ag salts <u>insoluble in 2M NH_3</u>
    Br^-, SCN^-, $[Fe(CN)_6]^{4-}$, I^-, S^{2-}

Group reactions of anions

B. Redox reactions: MnO_4^-, I^-, I_2 ; colour transitions

- I. Oxidation reactions of permanganate
  - Discoloration of MnO_4^- in acid medium (1M H_2SO_4) by action of ions wit reduction capability

    SO_3^{2-}, $S_2O_3^{2-}$, AsO_3^{3-}, S^{2-}, $[Fe(CN)_6]^{4-}$, Br^-, I^-, CN^-, SCN^-, NO_2^-

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + H_2O$$

$$5SO_3^{2-} + 2MnO_4^- \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$$

$$5S_2O_3^{2-} + 8MnO_4^- + 14H^+ \rightarrow 10SO_4^{2-} + 8Mn^{2+} + 7H_2O$$

$$5AsO_3^{3-} + 2MnO_4^- + 6H^+ \rightarrow 5AsO_4^{3-} + 2Mn^{2+} + 3H_2O$$

$$5S^{2-} + 2MnO_4^- + 16H^+ \rightarrow 5S + 2Mn^{2+} + 8H_2O$$

$$5\left[Fe\left(CN\right)_6\right]^{4-} + MnO_4^- + 8H^+ \rightarrow 5\left[Fe\left(CN\right)_6\right]^{3-} + Mn^{2+} + 4H_2O$$

$$5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$$

$$Hal.:\left(X^-\right)\ 10X^- + 2MnO_4^- + 16H^+ \rightarrow 5X_2 + 2Mn^{2+} + 8H_2O$$

Group reactions of anions

- II. Oxidation reactions of iodine
  - discoloration of I_2 in neutral or weakly acid (pH < 9) medium, reversible reaction ($NaHCO_3$ solid)

    SO_3^{2-}, $S_2O_3^{2-}$, AsO_3^{3-}, S^{2-}, $[Fe(CN)_6]^{4-}$, CN^-, SCN^-

$$I_2 + 2e^- \rightarrow 2I^-$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \ (tetrathionan)$$

$$CN^- + I_2 \rightarrow ICN + I^-$$

$$SO_3^{2-},\ AsO_3^{3-},\ S^{2-},\ [Fe(CN)_6]^{4-} - \ as\ with\ MnO_4^-$$

Group reactions of anions

- III. Reduction reactions of iodide
  - Anions with oxidation capability oxidize in acid medium iodide to iodine⟶ yellow, red-brown coloration of solution, blue coloration of starch solution

    CrO_4^{2-}, $Cr_2O_7^{2-}$, AsO_4^{3-}, S^{2-}, $[Fe(CN)_6]^{3-}$, NO_2^-

$$2CrO_4^{2-} + 6I^- + 16H^+ \rightarrow 2Cr^{3+} + 3I_2 + 8H_2O$$

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$AsO_4^{3-} + 2I^- + 2H^+ \rightarrow AsO_3^{3-} + I_2 + H_2O$$

$$2[Fe(CN)_6]^{3-} + 2I^- \rightarrow 2[Fe(CN)_6]^{4-} + I_2$$

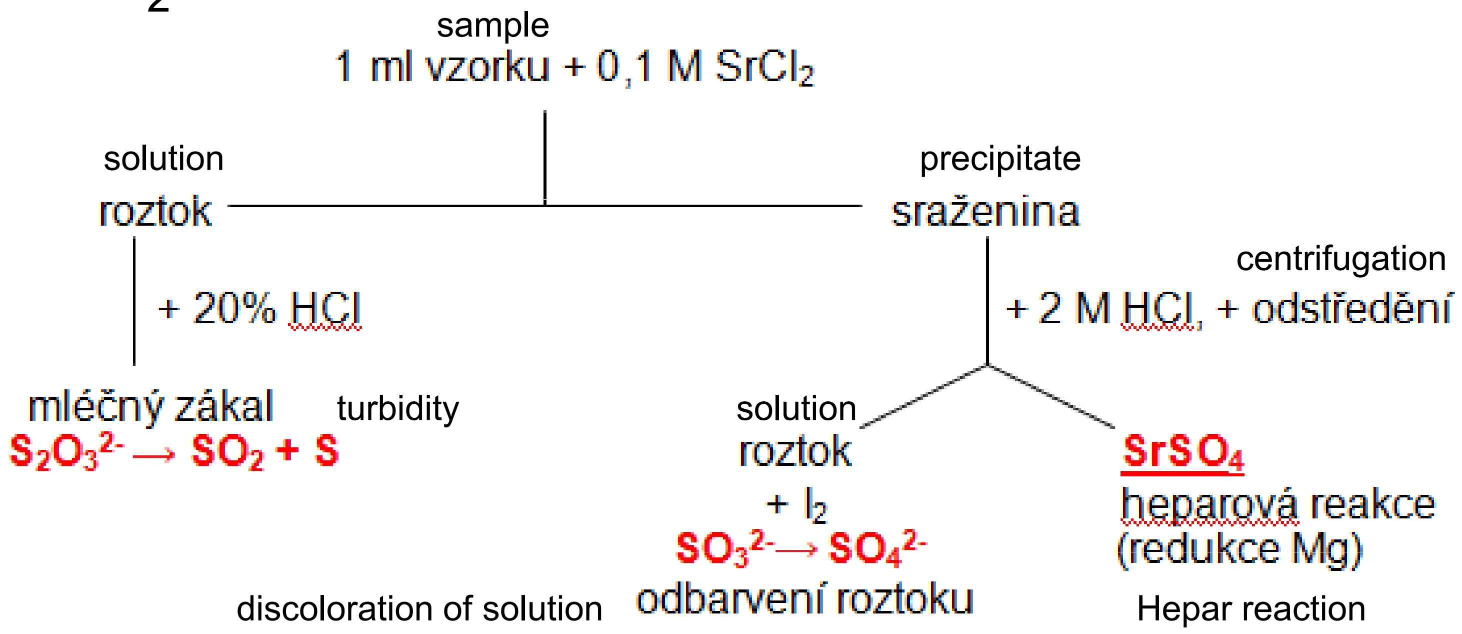
$$2NO_2^- + 2I^- + 4H^+ \rightarrow 2NO + I_2 + 2H_2O$$

Selective reactions of anions

- I. Group of low soluble Ba salts

$BaSO_4$ insoluble X BaS_2O_3 (decomposition→ SO_2, S – turbidity)

separation: $SrCl_2$



sample

1 ml vzorku + 0,1 M $SrCl_2$

solution

roztok

+ 20% HCl

mléčný zákal

turbidity

$S_2O_3^{2-} \longrightarrow SO_2 + S$

precipitate

sraženina

centrifugation

+ 2 M HCl, + odstředění

solution

roztok

+ I_2

$SO_3^{2-} \longrightarrow SO_4^{2-}$

odbarvení roztoku

discoloration of solution

$SrSO_4$

heparová reakce

(redukce Mg)

Hepar reaction

$BaSO_4$, $SrSO_4$ – detection of SO_4^{2-} by hepar reaction

Group of low soluble Ba salts

- **SO_4^{2-}**
  - precipitate, at heat with Mg → reduction

    resulting S^{2-} - detection: **PbAc** (lead acetate), black

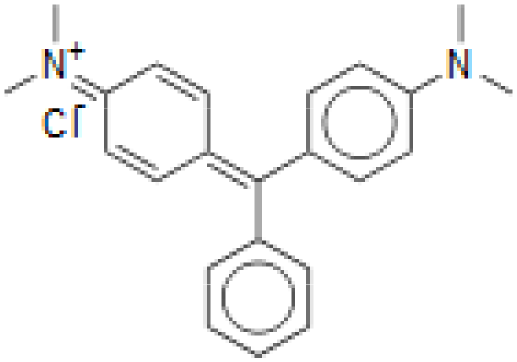
    $Na_2Fe(CN)_5NO$ (sodium nitroprusside)

$$\left[Fe^{III}(CN)_5NO\right]^{2-} + S^{2-} \rightarrow \left[Fe^{III}(CN)_5NOS\right]^{4-} \quad purple\ in\ alkaline\ medium.$$

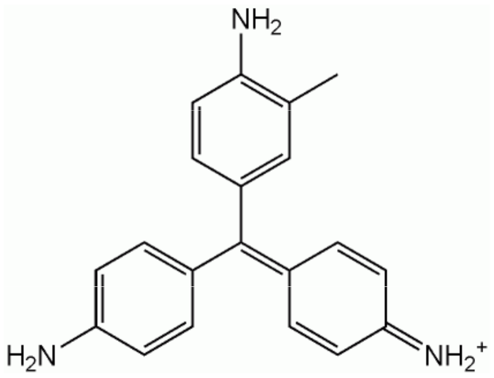
Group of low soluble Ba salts

- **SO_3^{2-}**
  - 1) with malachite green and fuchsin (Votoček)

malachite green



fuchsin



discoloration of solution (pH 7-12) formed sulfonanes

- ❑ interfere: S^{2-} and excess of (OH^-) pH > 12

  S^{2-} removing by means of $CdCO_3$, $ZnCO_3$

Group of low soluble Ba salts

- 2) with zinc nitroprusside – detection in gaseous phase

  $$SO_3^{2-} + 2H^+ \rightarrow H_2SO_3 \rightarrow SO_2 + H_2O$$

  $$Zn[Fe(CN)_5NO] \rightarrow Zn_2[Fe(CN)_5(NO)SO_3]$$

  sulphites nitroprusside Zn
  (red, low soluble)

  - interferes: $S_2O_3^{2-} \xrightarrow{H^+} SO_2 + S^{2-}$
  - masking: $HgCl_2$
  - procedure: on filtration paper soaked with reagent – above crucible in vapours. Unreacted nitroprusside is discoloured in ammonia vapour → only colour of product

Group of low soluble Ba salts

- **$S_2O_3^{2-}$**
  - 1) in acid medium decomposition:

$$H_2S_2O_3 \rightarrow H_2SO_3 + S \quad (colloid\ sulphur)$$

$$H_2SO_3 \rightarrow H_2O + SO_2$$

  - 2) with iron chloride

$$Fe^{3+} + S_2O_3^{2-} \rightarrow [Fe(S_2O_3)]^{+} \quad solution\ of\ purple\ complex$$

temporary colour because of reduction $Fe^{III} \rightarrow Fe^{II}$

$$2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{2+} + S_4O_6^{2-}$$

    - ❑ interfere: SCN^-, SO_3^{2-}
  - 3) iodazide reaction – catalysis; in presence of S^{2-} (included in $S_2O_3^{2-}$) fast reaction:

$$2N_3^- (sodium\ azide) + I_2 \rightarrow 3N_2 + 2I^- \quad red\ solution\ discolours$$

    - ❑ interfere: SCN^-, S^{2-} (separation as CdS, ZnS)

Group of low soluble Ba salts

- **F^-**
  - with <u>Zr^{IV}-chelate</u> with <u>xylenol orange</u>
    - More stable complex of Zr with ligands F^- → chelate is decomposed → red-purple chelate → yellow released reagent
    - Generally: use of F^- as strongly complexing agent

Group of low soluble Ba salts

- **SiO_3^{2-}**
  - s ammonium molybdate→ molybdate-silicic acid $H_4[Si(Mo_3O_{10})_4]$
    - originates in acid meduim – yellow solution
    - before smaple must alkalized, in order to obtain $Si(OH)_4$
    - by reduction with $SnCl_2$, $S_2O_3^{2-}$ → molybdenum blue – can be oxidized by HNO_3 to yellow $H_4[Si(Mo_3O_{10})_4]$
    - interfere: AsO_4^{3-}, PO_4^{3-} → molybdate-phosphoric acid and molybdate- arsenic acid

Group of Ag salts soluble in 2 M HNO_3

Soluble in 2 M HNO_3

- Coloration of salts: characteristic
  - Ag_2CrO_4 – russet, red-brown
  - Ag_3AsO_4 – chocolate brown
  - Ag_3PO_4, $AgAsO_2$ – yellow
  - $AgBO_2$ – white
  - Ag_2CO_3 – yellowish

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

neutral, alkal., yellow sol. **acid**, orange sol.

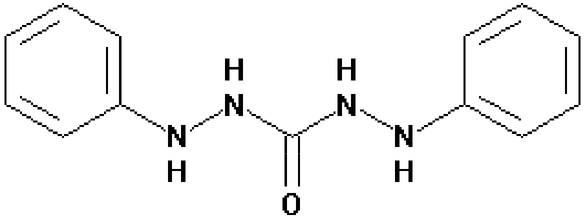
$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O \quad (acid \rightarrow alkaline)$$

interference: AsO_4^{3-} x PO_4^{3-} by molybdate NH_4^+

AsO_2^- (HNO_3 conc.) → AsO_4^{3-} the same

Group of Ag salts soluble in 2 M HNO_3

- **CrO_4^{2-}, $Cr_2O_7^{2-}$**
  - 1) <u>with hydrogen peroxide</u> (viz Cr^{3+}), acid medium
  - 2) <u>with benzidine</u> → semiquinone of benzidine blue
    - interfere: VO_2^+, MoO_4^{2-} and generaly oxidizing agents, acid medium
  - 3) with diphenylcarbazide → red-purple chelate with Cr^{III}, acid nto amylalcohole



    - interfere: Hg^{2+}, Fe^{3+}, MoO_4^{2-}, VO_4^{3-}
  - 4) with chromotropic acid→ purple-red solution in acid m.

Group of Ag salts soluble in 2 M HNO_3

- **PO_4^{3-}**
  - 1) with ammonium molybdate → yellow precipitate
    - x SiO_3^{2-} (yellow solution)
      $(NH_4)_3[As(Mo_3O_{10})_4]$
      ammonium tetrakis-trimolybdato phosphate
  - ☐ precipitation at hot , acid medium
  - ☐ interferes: AsO_4^{3-}
  - ☐ removing of AsO_4^{3-} by reduction with Zn powder to AsO_3^{3-} a and precipitation by H_2S na As_2S_3

$$AsO_4^{3-} + Zn + 2H^+ \rightarrow AsO_3^{3-} + Zn^{2+} + H_2O$$

Group of Ag salts soluble in 2 M HNO_3

- **$As^{III}O_2^-$ ($As^{III}O_3^{3-}$)**
  - 1) by reduction with $SnCl_2$ – common reaction with AsO_4^{3-}

    $$2AsO_2^- + 3SnCl_4^{2-} + 8HCl \rightarrow 2As^0 + 3SnCl_6^{2-} + 4H_2O + 2Cl^-$$

    (Bettendorf test)
  - 2) with sulphane → As_2S_3 yellow, As^V does not react!
- **$As^VO_4^{3-}$**
  - 1) by reduction with $SnCl_2$ – jako As^{III} → brownish As

    $$2AsO_4^{3-} + 5SnCl_4^{2-} + 16HCl \rightarrow 2As^0 + 5SnCl_6^{2-} + 8H_2O + 6Cl^-$$
  - 2) with ammonium molybdate → yellow precipitate

    $(NH_4)_3[As(Mo_3O_{10})_4]$ in acid medium HNO_3
    - ☐ interferes: PO_4^{3-}

Group of Ag salts soluble in 2 M HNO_3

Differentiation $As^{III}O_2^-$ x $As^{V}O_4^{3-}$ $AgNO_3$

$As^{III}O_2^-$: yellow precipitate Ag_3AsO_3 soluble in HNO_3 and NH_3

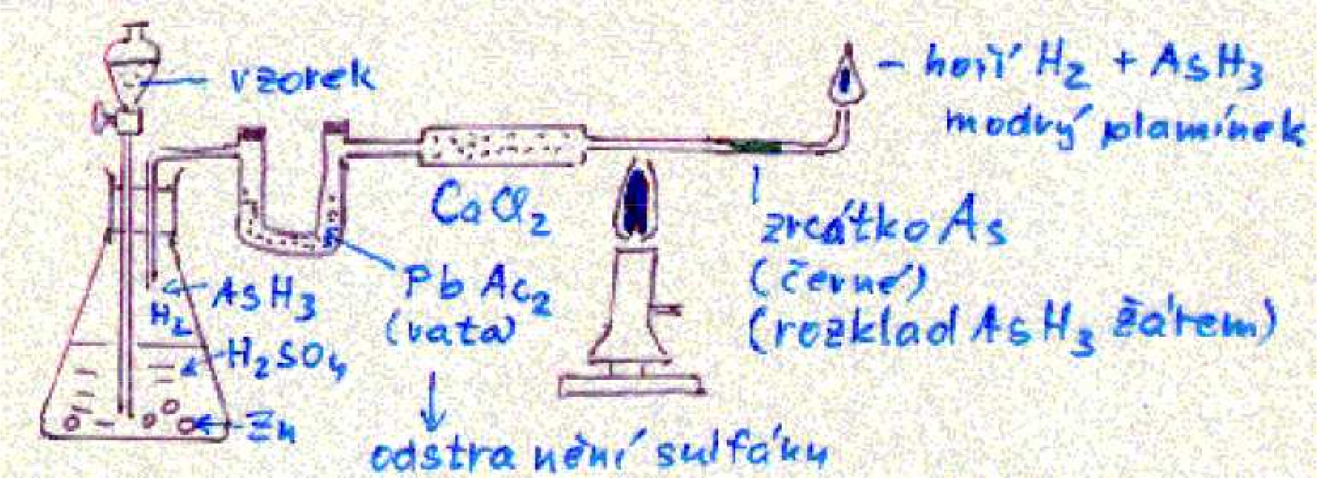
$As^{V}O_4^{3-}$: chocolate brown Ag_3AsO_4 soluble in HNO_3 and NH_3

As – toxicity, poisons, criminalistics

Common reactions of As– reduction to arsan (arsin) AsH_3

- 1) Marsh – Liebig test – official evidence

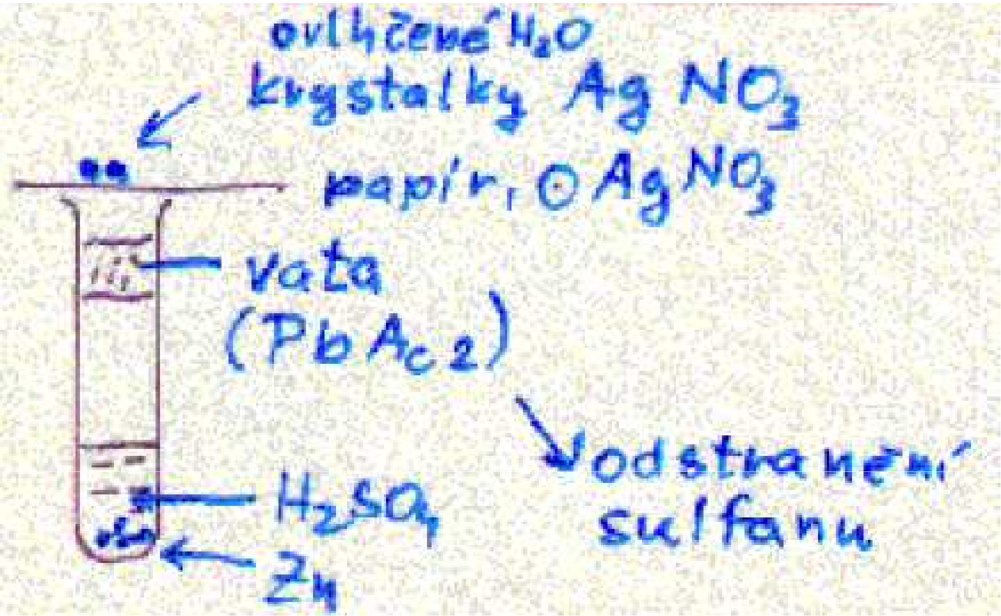
$$\left(As^{V}, As^{III}, As^{0}\right) + Zn \xrightarrow{H^{+}, H_2SO_4} Zn^{2+} + AsH_3\left(plyn\right)$$



As – toxicity, poisons, criminalistics

- 2) Gutzeit test– AsH_3
  - AsH_3 discolours paper with $AgNO_3$ yellow (arsenide Ag_3As) and than turns black due to decomposition

$$AsAg_3 \cdot AgNO_3 \leftrightarrow 6Ag + H_3AsO_3 + 3HNO_3$$



Group of Ag salts soluble in 2 M HNO_3

- **$B(OH)_4^-$**

  borate anion: $B(OH)_3 + H_2O \leftrightarrow HB(OH)_4$

  Monohydric acid pK = 10

  - 1) flame test – green flame (λ=548,1 a 519,3 nm)
    - interferes: Cu^{2+}
  - 2) flame test of volatile esters – green flame

    $B(OH)_3 + 3C_2H_5OH \leftrightarrow B(OC_2H_5)_3 + 3H_2O$
  - 3) with curcumin (curcumin paper)
    - Red soluble complex 1:1 in weak acid medium (red-brown discoloration of paper, blank – yellow), drop of alkaline hydroxide → dark green

Group of Ag salts soluble in 2 M HNO_3

- **CO_3^{2-}**
  - 1) with mineral acids

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

$$CO_2 + Ba(OH)_2 \rightarrow BaCO_3 \downarrow + H_2O$$

  - interferes: SO_3^{2-}, $S_2O_3^{2-}$, HS^-, CN^- → plyny
  - removing: decomposition by chromosulfuric acid (K_2CrO_4 v H_2SO_4)

    → oxidation of interfering anions to nonvolatile salts

    (also $KMnO_4$)

Group of Ag salts insoluble in 2 M HNO_3

- in 2 M HNO_3 precipitate:
  - AgCl, AgSCN – white
  - AgBr – yellowish
  - AgI – yellow
  - Ag_2S – black

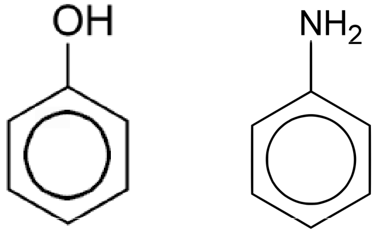
    - ❑ Cl^-, Br^-, SCN^- - stable in H^+, OH^-
    - ❑ I^- v H^+oxidation → I_2 (yellow)
    - ❑ HS^-, S^{2-} - hydrolysis→ H_2S, polysulphides

- ❑ E_0 – standard potentials of redox reactions

$$Cl_2 / 2Cl^- \approx +1{,}36\ V, Br_2 / 2Br^- \approx +1{,}07\ V, I_2 / 2I^- \approx +0{,}58\ V$$

Group of Ag salts insoluble in 2 M HNO_3

- **Cl^-**
  - 1) $Ag^+ + Cl^- \rightarrow AgCl \downarrow \qquad AgCl \downarrow + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$
  - 2) <u>with Deniges reagent</u> (mixture of phenol and aniline)

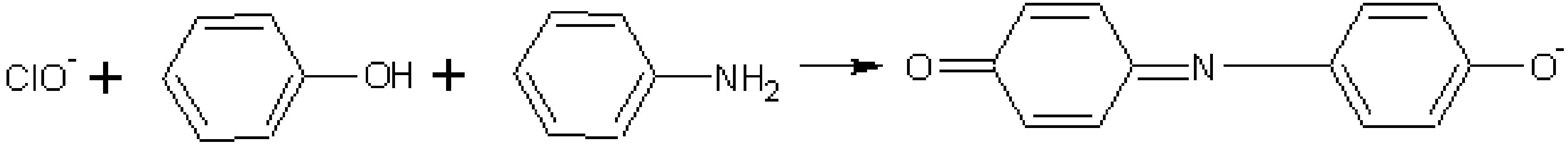


- ❑ In conc. H_2SO_4 Cl^-

is oxidized by $KMnO_4$ to Cl_2

$$2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 5Cl_2 + 8H_2O + 2Mn^{2+}$$

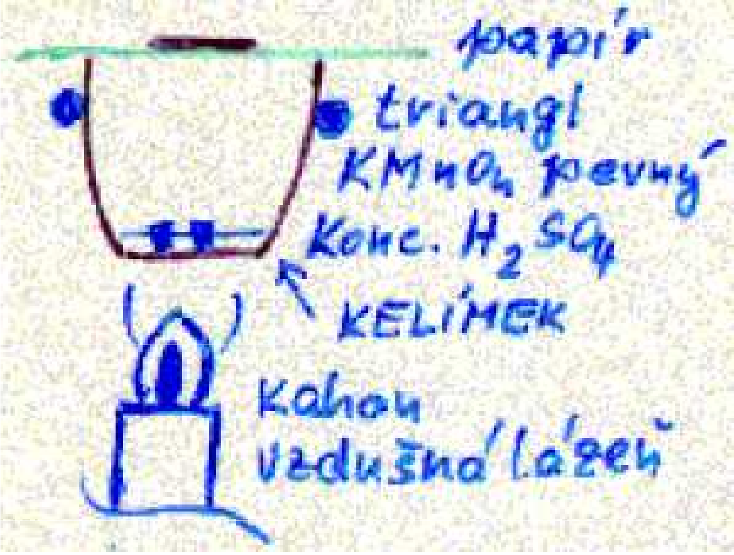
$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O(disproporcion.)$$



indofenol (modry v OH⁻ prostredi)

- ❑ + drop of 1 M NaOH, drop of Deniges reagent

Group of Ag salts insoluble in 2 M HNO_3



- also with pipette: above crucible pipette with NaOH – absorption of $Cl_2 \rightarrow ClO^-$
- blow out on the drop board with Deniges reagent
- dry part of paper colours brown, purple
- do not transferred BrO^-, IO^- !

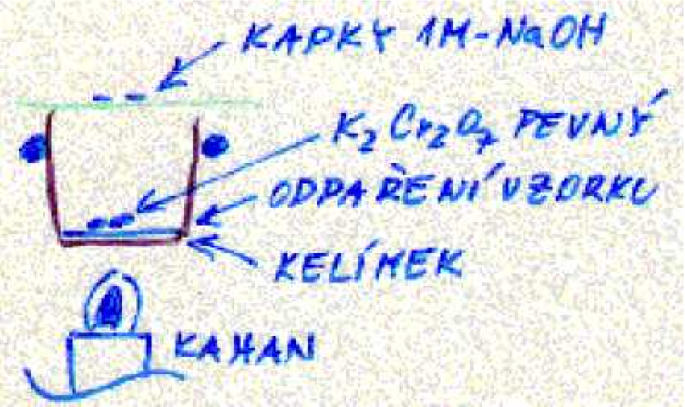
Group of Ag salts insoluble in 2 M HNO_3

- 3) <u>chromylchloride formation</u>
  - In anhydrous medium (conc. H_2SO_4)

$4Cl^{-} + Cr_2O_7^{2-} \leftrightarrow 2CrO_2Cl_2 + 3H_2O$ (red-brown, volatile)

  - on paper reaction with OH^-

$CrO_2Cl_2 + 4OH^{-} \leftrightarrow CrO_4^{2-} + 2Cl^{-} + 2H_2O$



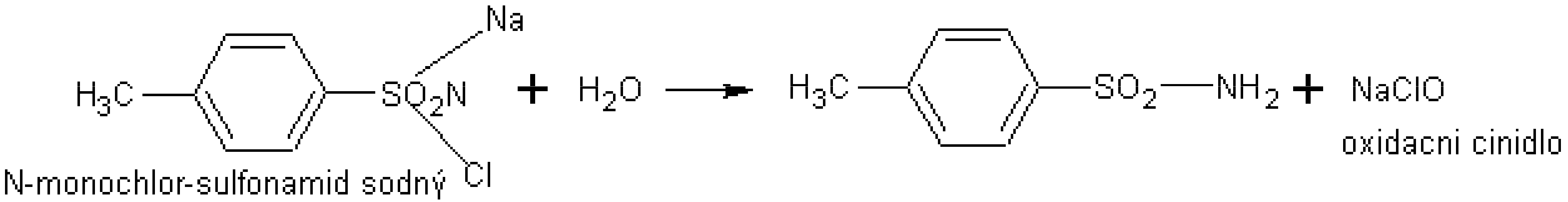
paper discolurs yellow
by chromate

$6Br^{-}\left(I^{-}\right) + Cr_2O_7^{2-} + 14H^{+} \leftrightarrow 2Cr^{3+} + 3Br_2\left(I_2\right) + 7H_2O$

  - interferes: NO_2^-, NO_3^- → NOCl

Group of Ag salts insoluble in 2 M HNO_3

- **Br^-**
  - 1) <u>oxidation to Br_2 by chloramine T</u>



- ❑ Br_2 – yellow, discolorates brown – extraction to $CHCl_3$
- ❑ interfere: SCN^-, I^- (excess)
- ❑ In presence of I^- oxidation to I_2 at first (brown discoloration of aequous phase – purple in CCl_3H), then $I_2 \rightarrow IO_3^-$ (colourless) and then Br_2

  $SCN^- \rightarrow (CN)_2$ – dikyane - poisonous

Group of Ag salts insoluble in 2 M HNO_3

- **I^-**
  - 1) oxidation to I_2 by sodium nitrite

    $$2I^- + NO_2^- + 2H^+ \rightarrow I_2 + H_2O + NO$$

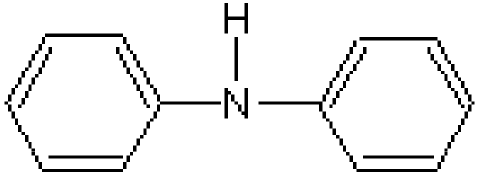
    - ❑ DetectionI_2: a) extraction to CCl_4 or $CHCl_3$ – purple solution
      b) starch solution – blue
      c) iodide-starch paper- blue
    - ❑ interferences: $S_2O_3^{2-}$
- **SCN^-**
  - 1) with $CeCl_3$ – in acid medium
    - ❑ interferes: F^-, $H_2PO_4^-$ (excess) $[FeNCS]^{2+}$ $[Fe(NCS)_2]^+$ red complex
- **HS^-, S^{2-}**
  - 1) with Pb^{2+} →PbS
  - 2) with nitroprusside → $[Fe^{II}(CN)_5NOS]^{4-}$ purple complex

Group NO_3^-, NO_2^-, ClO_4^-

- **NO_3^-, ClO_4^-**
  - in solutions stable oxidative properties
  - Do not form: complexes, precipitates
    - NO_3^- analogy to Na^+ - soluble salts
    - ClO_4^- large volume, small charge, formation of ionic associates with basic organic dyes
- **NO_2^-**
  - oxidative properties ($2\ I^- \rightarrow I_2$)
  - oxidized by atmospheric O_2 to NO_3^-

Group NO_3^-, NO_2^-, ClO_4^-

- **NO_3^-**



  - 1) with diphenylamine
    - blue oxidation product (v konc. H_2SO_4)
    - interferes: NO_2^-, CrO_4^{2-}, MnO_4^- (oxidation reagents), Fe^{3+}, I^-, IO_3^- (formation of I_2)
  - 2) formation of azodye after reduction by Zn na NO_2^-
    - in Hac is NO_3^- reduced by pulver Zn to NO_2^-
    - detection by diazotation and coupling reaction by formation of azodye
    - Interferes : NO_2^- → removing by:

a) urea in 1 M H_2SO_4

$$2HNO_2 + CO(NH_2)_2 \rightarrow 2N_2 + CO_2 + H_2O$$

b) potassium iodide in Hac (80%)

$$2NO_2^- + 2I^- + 4H^+ \rightarrow 2NO + I_2 + 2H_2O$$

Group NO_3^-, NO_2^-, ClO_4^-

c) sodium azide (weak acid media)

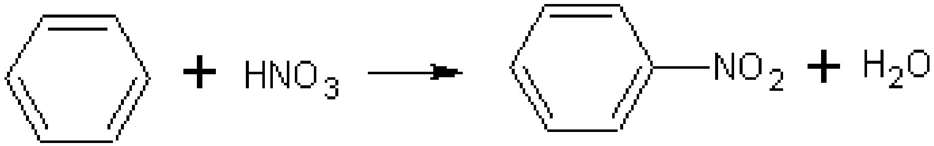
$$HN_3 + NO_2^- + H^+ \rightarrow N_2 + N_2O + H_2O$$

d) ammonium salts (acid medium)

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

side reaction !!! : 3 $HNO_2 \rightarrow HNO_3 + 2NO + H_2O$

- 3) <u>nitration reactions</u> – in acid medium (conc. H_2SO_4)
  - yellow to orange comp. character. smell (blank necessary)



  - NO_2^- does not interfere – only H_2SO_4 discolours orange
  - interferes: I^- → removing by precipitation with $PbAc_2$
  - Nitration of other componds: phenolsulfonic acid, phenol-2,4-disulfonic acid, α-naphtolsulfonic acid, α-naftylamin (red-purple) pyrocatechol (green), m-phenylendiamien (žl.,červený), chromotropic acid

Group NO_3^-, NO_2^-, ClO_4^-

- 4) reduction reaction – by Zn or Devard alloy (Cu – Zn - Al) in alkaline medium → NH_3 = reduction by nascent hydrogen

$3\ NO_3^- + 8\ Al + 5\ OH^- + 18\ H_2O \rightarrow 3\ NH_3 + 8\ [Al(OH)_4]^-$

interfere: NO_2^-, CN^-

  - direct detection: nitration after removing of halogenides by silver sulfate
  - Proceedure for reduction reactions:

a) positive reaction with diphenylamine (proof of oxidation properties)

b) reduction by Zn in OH^- medium rises NH_3 (nitrogen proof)

c) by means of KI to verify possible presence of NO_2^- and by positive reaction to remove

d) By reducing with Zn in HAc convert NO_3^- to HNO_2 and NO_2^- detect by formation of azodye

Group NO_3^-, NO_2^-, ClO_4^-

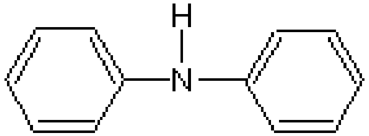
- **NO_2^-**

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \quad (unstable\ acid)$$

  - 1) <u>with KI – oxidation of I^- to iodine</u>

$$2NO_2^- + 2I^- + 4H^+ \rightarrow 2NO + I_2 + 2H_2O$$

    - it is evidence of NO_2^- along with the presence of NO_3^-
    - instant reaction unlike with $Cr_2O_7^{2-}$ or ClO_3^-
  - 2) <u>with diphenylamine</u> <u>oxidation to d. blue</u>

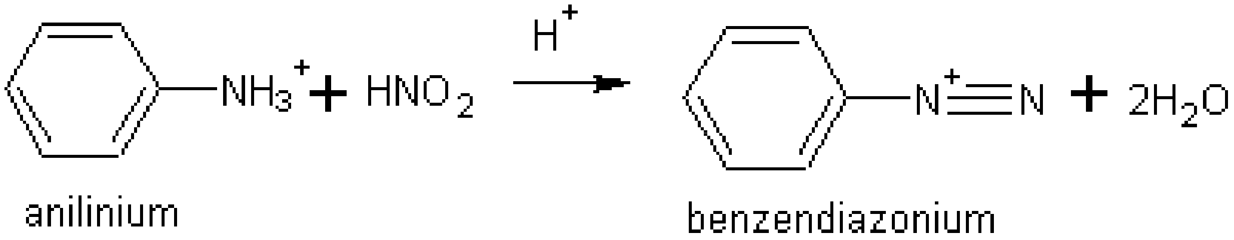


    - interferes: NO_3^-, $Cr_2O_7^{2}$
  - 3) <u>with $KMnO_4$</u> – reduction to Mn^{2+}

$$5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$$

Group NO_3^-, NO_2^-, ClO_4^-

- 4) diazotation reaction of HNO_2 and coupling to azodyes
  - diazotation



  - coupling

    in H^+ with aromatic amine