2008

Reactions recommended for the identification of compounds

Compound	Phenomena resulting from the interaction with the reagents					
	NaOH	$KMnO_4$ (neutral)	$KMnO_4$ (alkaline)	$FeCl_3$	$NaNO_2$ + HCl	*p*-DMABA + HCl
Analgin	No changes	Instantaneous reduction	Reduction	Vanishing blue color	Blue color changing into pale-yellow	Yellow
Streptocide		**No reaction**		No changes	Very slowly turning yellow	**Brick-red**
Paracetamol		Instantaneous reduction		Practically no changes	**Yellow color**	Yellow
Acetylsalicylic acid		Very slow		**Very weak color**	No changes	No changes
Salicylic acid		Rapid reduction		**Bright-purple color**		
Benzoic acid		**No reaction**	**No reaction**	No changes		
p-Nitrophenol	**Yellow color**	Slow reduction	Reduction	Purple color		

Comments to the Table above.

- *p*-Nitrophenol is identified by the yellow color of phenolate ion
- Benzoic acid is identified by non-reduction of the alkaline permanganate (one will only need to distinguish it from streptocide, if neutral permanganate is used).
- Streptocide is identified by intense color of the reaction product with *p*-DMABA (analgin and paracetomol give weaker coloration).
- Salicylic acid is identified by coloration with iron(III) (the color is most intense in the case of chelate formation, which is possible only for salicylate).

- Aspirin (acetylsalicylic acid) gives the same reaction, still with much weaker coloration (the latter is due to salicylic acid admixture or slow hydrolysis of aspirin affording salicylic acid). By contrast to paracetamol, aspirin is not nitrated by nitrite.
- Paracetamol is identified by the formation of a yellow nitro-derivative (in acidic media, nitrite introduces a nitro group (earlier believed to be a nitrozo group) in the 2nd position of phenol). The coloration develops most promptly in the case of paracetamol rather than streptocide, which needs to be identified with *p*-DMABA.
- Analgin forms an intensely colored blue radical with all the oxidizers. The radical undergoes fast decomposition. By contrast to paracetamol, aspirin and salicylic acid, analgin does not form any stable products with iron(III) or nitrite. Analgin reduces neutral permanganate, which differs it from streptocide and correlates with the existence of a double bond in its structure.

1. Diazotization reaction:

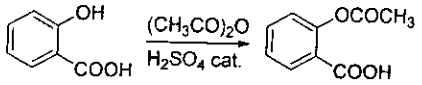
$$Ar\text{–}NH_2 + HNO_2 \rightarrow Ar\text{–}N{\equiv}N^+$$

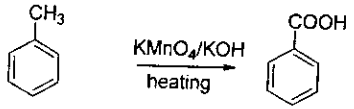
2. Formation of colored azo compounds (azo coupling reaction with phenols):

$$Ar\text{–}N{\equiv}N^+ + Ar'\text{–}OH \rightarrow Ar\text{–}N{=}N\text{–}Ar'\text{–}OH$$

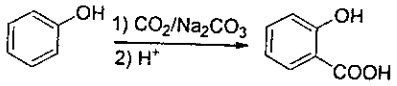
5. Distillation with water vapor can be used for separation because *o*-nitrophenol forms intramolecular hydrogen bond.

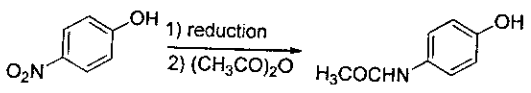
6.

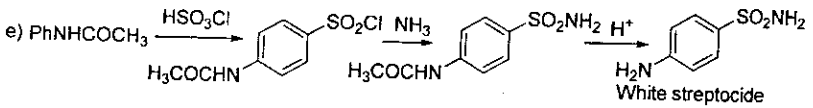
a) 

b) 

(other oxidants can be also used)

c) 

d) 

e) 

White streptocide

2009

Part 1. Identification of inorganic compounds

1–2. There can be different approaches towards the identification of compounds **1–10**. One of these is given hereunder. Using pH-indicator paper we can disclose the acidic solutions of sulfuric acid and aluminum salt, as well as an alkaline solution of potassium carbonate, and possibly a weakly alkaline nitrite solution (pH 7.5–8.0). Abundant precipitation of aluminum hydroxide observed on mixing of carbonate and aluminum salt allows identification of the acid, potash and aluminum(3+). Nitrite and acid mixture turns out to be a reagent usable to find the iodide solution, since the latter is oxidized to iodine by nitrite. Two solutions become cloudy when acidified with sulfuric acid: these are thiosulfate (precipitation of sulfur) and barium salt (precipitation of $BaSO_4$). Treatment of the rest solutions with a mixture of iodide and a sufficient amount of sulfuric acid allow attributing chlorate due to iodine formation. Thiosulfate and barium salt can be distinguished based on precipitation with sulfuric acid (slowly appearing cloudiness in the case of thiosulfate and an immediate process in the case of barium salt), as well as by the addition of the rest two unidentified solutions, NaCl and Na_2SO_4. The precipitate is formed only in the system containing barium salt and sodium sulfate.

Part 2. Determination of sulfate ion in ammonium sulfate

3. $NH_4^+ + R\text{–}SO_3^-H^+ \rightarrow R\text{–}SO_3^-NH_4^+ + H^+$.

4. $H^+ + CH_3COO^- \rightarrow CH_3COOH$

6. The molar mass of Alizarine red S is 360 g/mol; the concentration of 0.2 g/100 mL corresponds to $5.6 \cdot 10^{-3}$ M.

7. Washing of the column with a relatively high volume of water should elute all the exchanged protons. Taking into account the eluate volume (20 mL), the initial volume (5 mL) and the fact that all the ammonium ions have been exchanged to hydrogen ones, we find the sulfuric acid concentration as 0.1 M·5 mL / 20 mL = 0.025 M. Since the acidity is not high, the sulfuric acid would undergo dissociation at both steps. Thus, the proton concentration can be accepted equal to 0.05 M, and $pH_1 = 1.30$ (a more precise calculation accounting for the second dissociation constant equal to 0.01 results in the pH value equal to 1.37).

Addition of sodium acetate brought the solution volume up to 27.5 mL. The amount of the acetate added: 0.1 M ·7.5 mL = 0.075 mmol, and the concentration: 0.075 / 27.5 = 0.027 M. The new proton concentration: 0.05·20 / 27.5 = 0.036 M. As a result, there will be an excess of protons of 0.036 – 0.027 = 0.009 M as well as acetic acid formed (0.027 M). Acetic acid can be treated as non-dissociating in