Lesson 1.
Chemical-toxicological analysis for a group of substances
Isolated by distillation. "Flying" poisons. Features of isolation.

Chemical-toxicological analysis of hydrocyanic acid derivatives

One method for isolating toxic substances is distillation from water vapor.

Using this method from biological material

There are many groups of substances (volatile poisons):

1. Hydrocyanic acid HCN
2. Aliphatic alcohols: methyl alcohol, ethyl alcohol, propanol, butanol, pentanol;
3. Diols: ethylene glycol;
4. Alkyl halides: chloroform, chloral hydrate, carbon tetrachloride, dichlorethane;
5. Aldehydes: formaldehyde;
6. Ketones: acetone;
7. Monohydric phenols and their derivatives: phenol, cresols;
8. Carboxylic acids: acetic acid;
9. Some alkaloids: nicotine, anabasine, pachycarpine

Steam distillation method.

- Steam distillation in chemical toxicological analysis is used to isolate toxic substances from various objects (vomit, food,internal organs).

- This method can be used to isolate substances with both low and high boiling points.
- Steam distillation lowers the boiling point of substances at which they can decompose. For example, tetraethyl lead decomposes at temperatures above 100°C. Its boiling point is 200°C, at which almost all of it decomposes. By steam distillation it is possible to isolate undecomposed tetraethyl lead.

Objects of forensic chemical research for the detection of "volatile poisons":

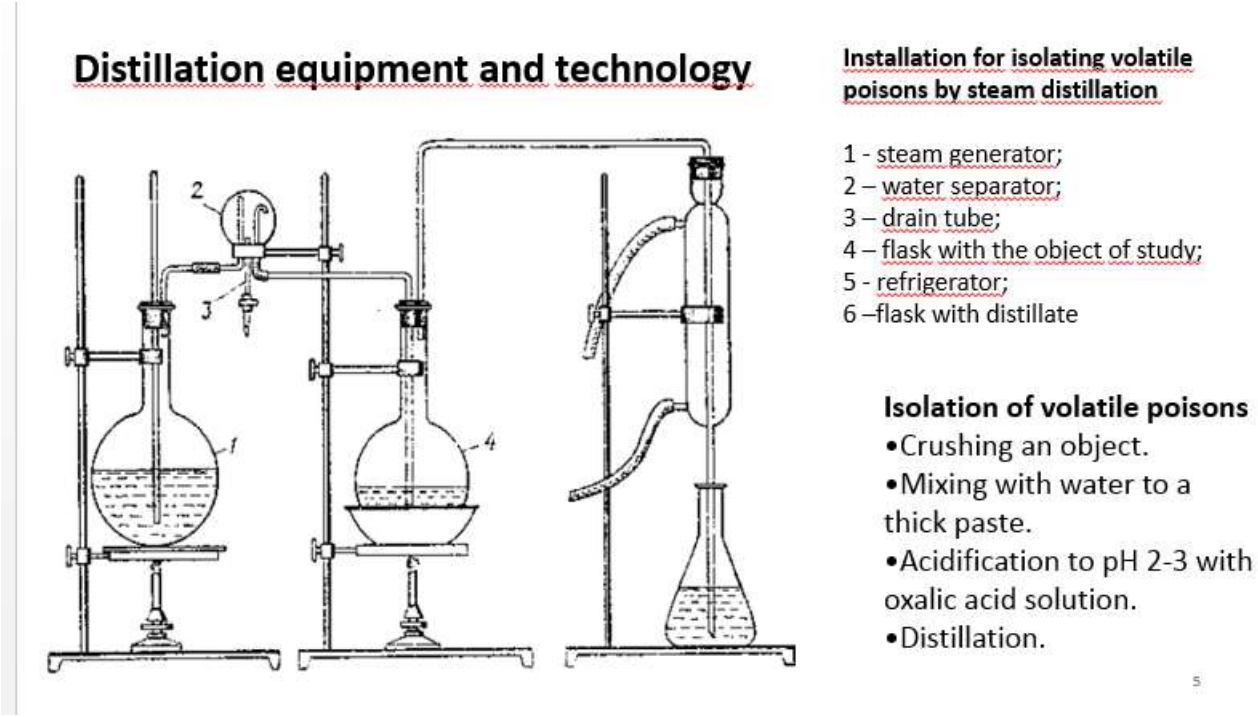
- internal organs of a corpse, blood, urine, vomit, food products.
- If poisoning with organochlorine substances is suspected, the omentum and 1/3 of the brain are additionally sent,

- methanol - 1/3 of the brain,
- ethanol - blood from large veins, urine, muscle tissue.

When conducting research on a group of "volatile" poisons, you need **to pay attention to**:

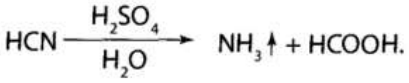
1. **Smell of the object**
2. **Smell and appearance of the distillate**

- oily drops on the surface of the distillate and characteristic irritating smell of fusel oil (amyl alcohols)
- - heavy drops at the bottom of the distillate and a sweetish smell - chloroform, dichloroethane, carbon tetrachloride.
- - Phenol - characteristic odor of carbolic acid, milky cloudiness, and pinkish droplets onat the bottom of the receiver due to phenol oxidation products.

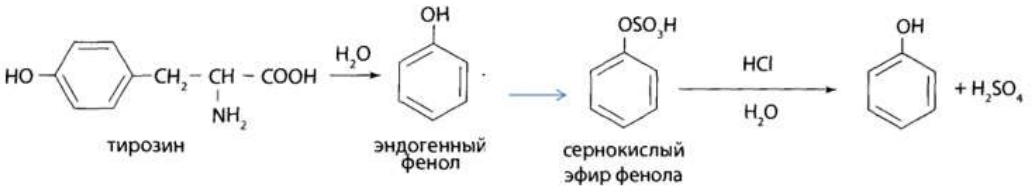


You cannot use strong mineral acids, because... this would result:

1) to the destruction of the HCN molecule (hydrolysis), which will lead to its loss and **under-discovery**:



2) to the **rediscover**y of phenol as a result of the hydrolysis of its sulfate esters, which are normal part of biological material:



Distillate collection:

Collect 3 distillates

- **The first portion of the distillate** in the amount of 3 ml is collected in 2 ml of a 5% sodium hydroxide solution (according to I.V. Gerasimova in a mixture of 2% solutions of sodium carbonate and sodium bicarbonate (1:1)).

In this case, hydrocyanic acid transforms into its salt, and its loss is prevented due to high volatility:

The entire volume of the first portion of the distillate is examined only for hydrocyanic acid.

The 2nd portion of the distillate is distilled off in a volume of 25-50 ml. It containssubstances of medium volatility (alcohols, acetone, alkyl halides and etc.).

The 3rd portion of the distillate is also collected in a volume of 25-50 ml. In it contains highly volatile substances (formaldehyde, ethylene glycol, etc.)

Hydrocyanic acid or prussic acid HCN

Sources of poisoning:

1. kernels of bitter almonds, apricots, cherries, cherry laurel and other plants of the family Rosaceae containing the glycoside **amygdalin**
2. **phaseolunatin** – glycoside of Indian beans (Phaseolus lunatus)
3. **linamarin** – flax seed glycoside
4. water manna containing a glycoside that splits off HCN
5. cyanogen [(CN)2], cyanogen chloride and bromide (ClCN, BrCN)
6. burning of celluloid, wool and polymer materials
7. HCN are found in tobacco smoke!

Entry into the body:

• with inhaled air,

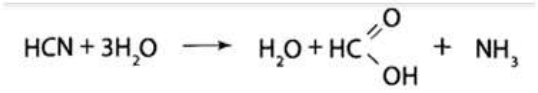
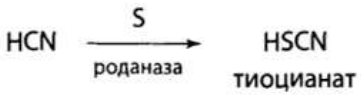
• absorbed through the skin,

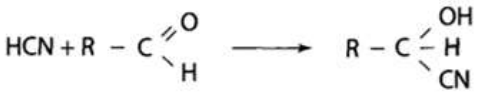
• through the digestive canal, through the gastrointestinal tract.

Mechanism of action:

Cyanides stabilize iron cytochrome oxidase intrivalent state, which completely disrupts cellularbreath. Tissue hypoxia occurs, despite the fact that the blood saturated with oxygen. The cells of the central nervous system are most sensitive to oxygen deficiency. In addition, cyanides disrupt the activity of more than 20enzyme reactions. This leads to rapid development of intoxication and rapid death.

Biotransformation of hydrocyanic acid

1. Hydrolysis 
2. Conversion into thiosionates under the influence of the enzyme rhodanase: 

3. Connection with blood hemoglobin.
4. Binding to cysteine.
5. Addition to substances containing an aldehyde group, for example sugars: 

Objects of analysis

1. **body of the living** take:

-blood, urine, vomiting

2 **forensic expertise (dead):**

- *1/3 liver, 1 kidney, stomach with contents, blood, urine*

3 non-biological objects*: food, liquids, crime scene powders, etc.*

The isolation method is steam distillation.

Collect the first distillate in 2 ml of 5% sodium hydroxide to prevent volatilization of hydrocyanic acid.

Detection

1. Prussian blue formation reactionafter 48 hours a blue color forms

$$NaOH + HCN = NaCN + H_2O$$

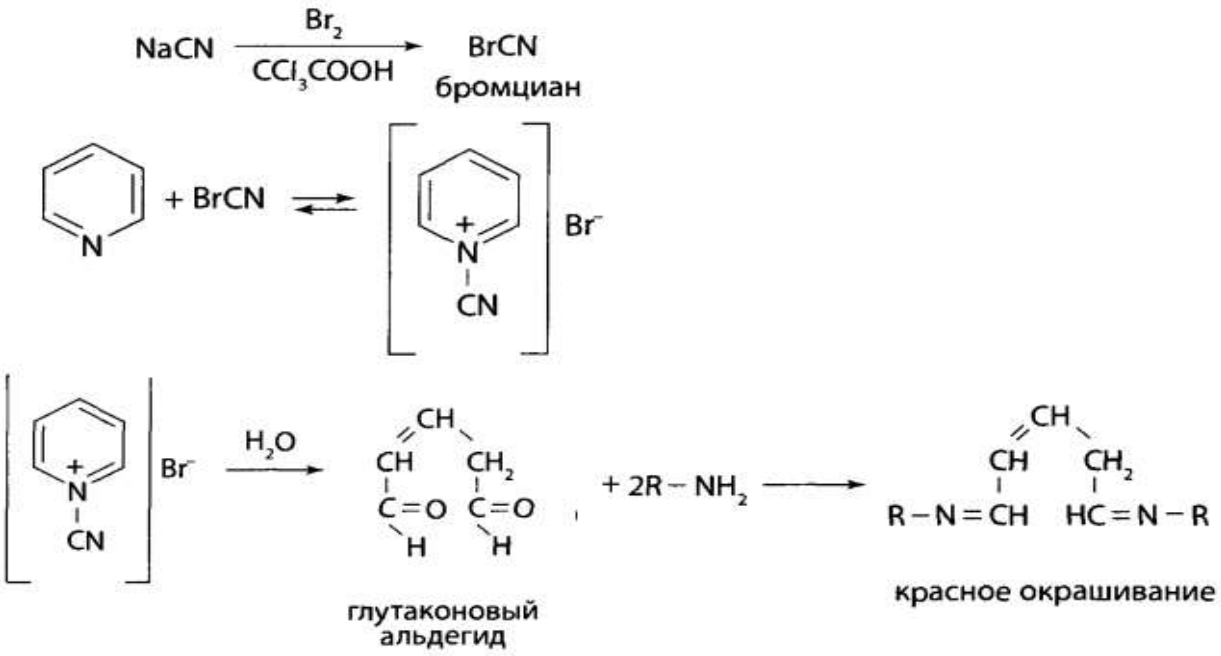
$$2NaCN + FeSO_4 = Fe(CN)_2 + Na_2SO_4$$

$$Fe(CN)_2 + 4NaCN = Na_4[Fe(CN)_6]$$

$$3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 = Fe_4[Fe(CN)_6]_3\downarrow + 6Na_2SO_4$$

2. The reaction of the formation of polymethine dye using a pyridinebenzidine reagent.

Add 0.5 ml of bromine water to part of the distillate, 1ml of 10% trichloroacetic acid solution, and then 0.5 ml of 0.5% hydrazine sulfate solution. 3 ml of pyridine-benzidine mixture is added to the solution. The formation of an orange color is observed, gradually turning into red-violet.



3. Microcrystalloscopic reaction of silver cyanide formation.

HCN + AgN0₃ -> AgCN + HN0₃

Quantitative assessment of hydrocyanic acid is carried out:

1. Photocolorimetric method
2. Titrimetric method.

$$AgNO_3 + NH_4CNS \rightarrow AgCNS\downarrow + NH_4NO_3$$

$$3NH_4CNS + NH_4Fe(SO_4)_2 \rightarrow Fe(CNS)_3 + 2(NH_4)_2SO_4$$

HCN + AgN0₃ -> AgCN + HN0₃