«General pharmaceutical chemistry »

OXIDIMETRY: BROMATOMETRY. NITRITOMETRY.

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Bromatometry

Bromatometry is a redox titration method, based on the reduction reaction of a bromate ion.

The basic reaction brom

$$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$$

If bromate ions are added to a solution of bromide ions in the presence of acid, molecular bromine is formed:

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

An aqueous solution of **potassium bromate** is used as a **titrant**.

Bromatometry

Types of bromatometry

1) Determinations based on the oxidation of the substance of interest with bromate in an acidic environment; the bromate ion is reduced to bromide:

$$BrO_3^- + 6H^+ + 6\bar{e} = Br^- + 3H_2O$$

2) Determinations based on the interaction of the substance of interest with bromine produced by the reaction of $KBrO_3$ with KBr in an acidic medium:

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O.$$

Definitions of the second kind are also called *bromometric*.

Bromatometry

Preparing a titrated solution of potassium bromate

A solution of potassium bromate can be prepared from an exact sample.

The standardisation of the $KBrO_3$ solution is carried out iodometrically. firstly the reaction of $KBrO_3$ with KI is conducted:

$$KBrO_3 + 6KI + 6HCl = 3I_2 + 6KCl + KBr + 3H_2O$$

and then titrate the released iodine with a standard solution of $Na_2S_2O_3$.

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

The standard solution of $KBrO_3$ is stable during storage.

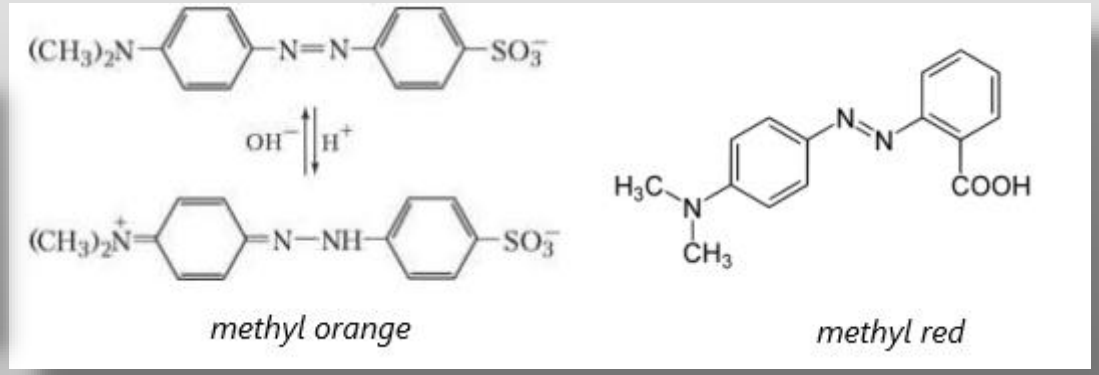
Bromatometry

Fixing the titration end point

The indication-free method

The endpoint in titration with $KBrO_3$ (or in cases of direct bromometric titration) is indicated by the appearance of free bromine in the solution. The release of bromine is indicated by a yellow colouring of the solution.

Indicators



Instrumental methods

The titration endpoint can also be detected potentiometrically or photometrically.

Bromatometry

Direct bromatometric titration

The direct bromatomeric determination is based on the equation for reducing bromates to bromides:

$$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$$

After all of the substance to be determined has reacted, the excess amount of titrant reacts with the bromide ions.

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

This produces Br2, which leads to the **disappearance** of the **methyl orange** colour.

Bromatometry

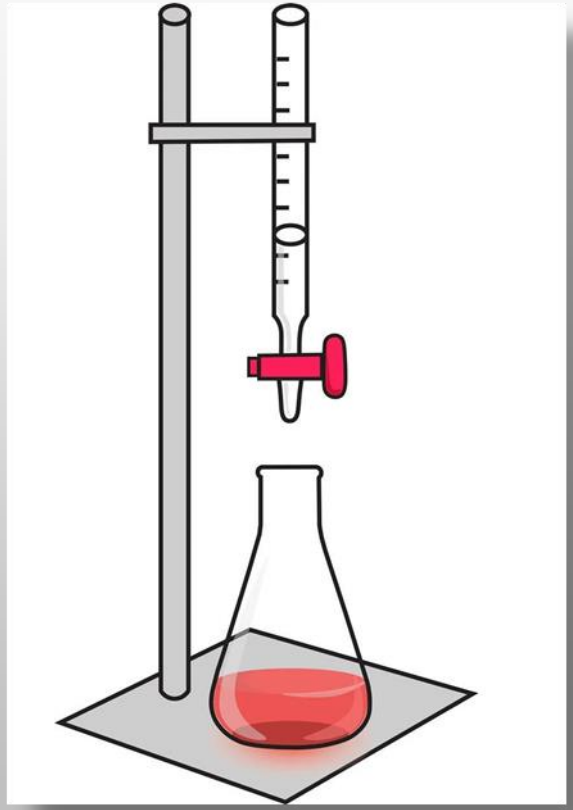
Bromometric (bromatometric) determination

Bromometric determinations are carried out in the presence of excess KBr which is added to a solution of the substance to be determined or to a titrant (Potassium bromate).

Only in an acidic medium!

Titration is based on reaction:

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

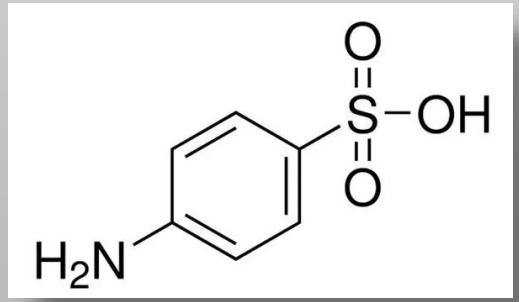


Bromatometry

Bromometric (bromatometric) determination

This type of titration is used to the determination of organic substances that undergo

- *electrophilic substitution reactions* (phenols, aromatic amines)
- *electrophilic addition* (organic substances with multiple bonds in the molecule) with bromine.

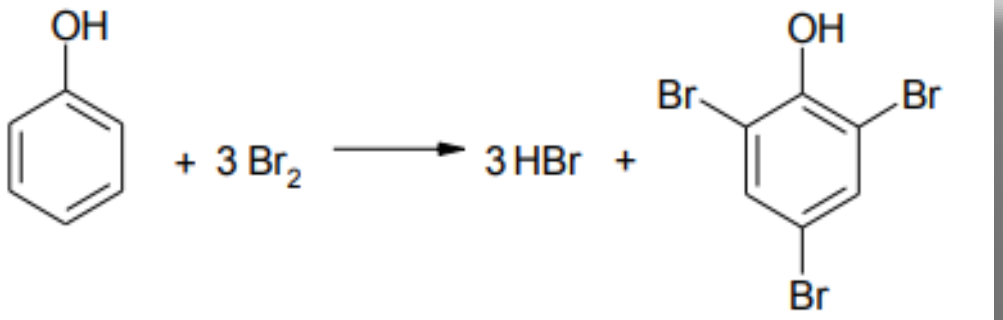


Bromatometry

Applications in pharmaceutical analysis

Direct bromometric titration

Phenol
Titrant $KBrO_3$
Indicator methyl orange

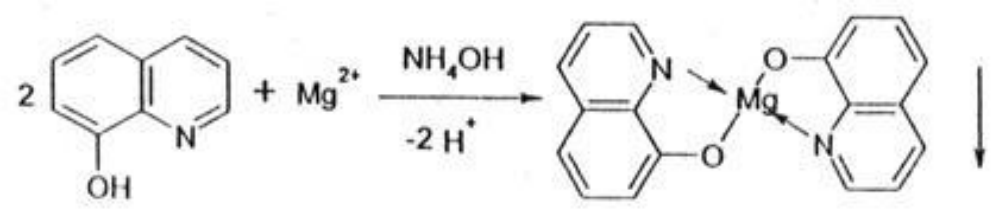


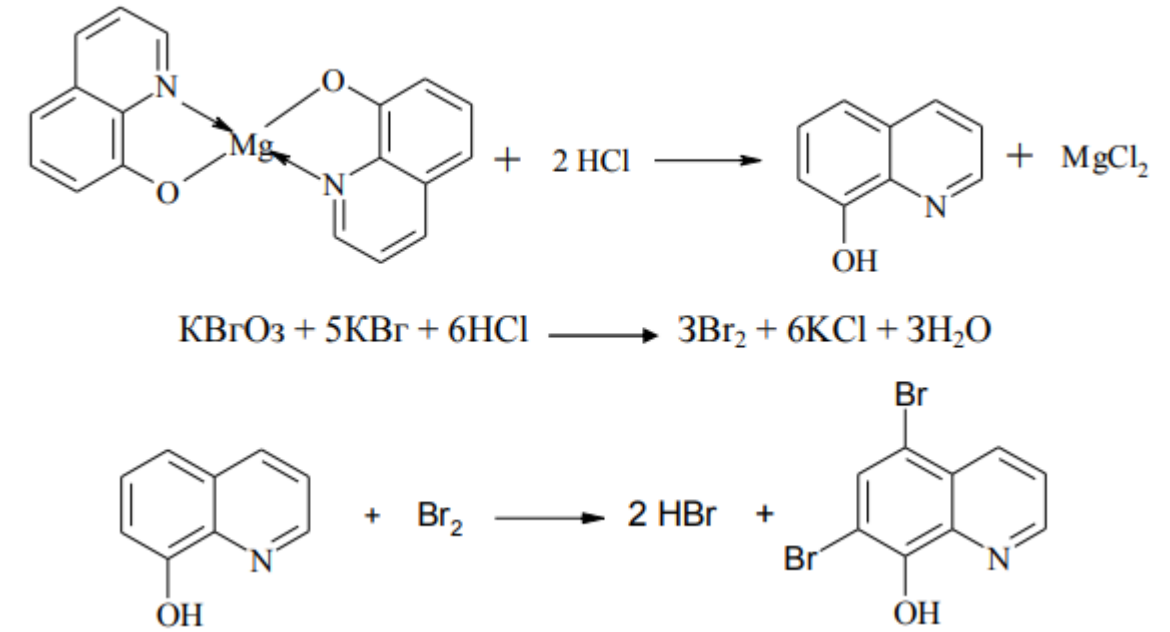
Bromatometry

Applications in pharmaceutical analysis

Indirect (substitution) bromometric titration

Magnesium salts
Titrant $KBrO_3$
Indicator methyl red





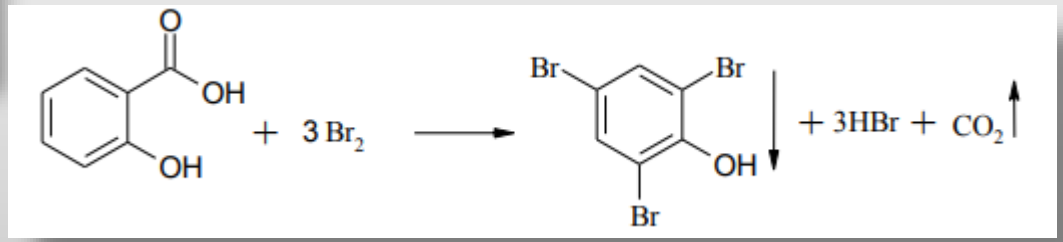
Bromatometry

Applications in pharmaceutical analysis

Reverse bromometric titration (bromide–bromate determina

Salicylic acid
Titrant sodium thiosulphate **Indicator** starch

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + 3H_2O$$



$$2KI + Br_2 \rightarrow 2KBr + I_2$$

$$Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Bromatometry

Advantages

- Widespread use
- Stability of the potassium bromate solution during storage and accuracy of analysis

Bromatometry

Disadvantages

1. Water present in solution or produced during titration of non-aqueous solutions interferes with the determination of many organic compounds.
2. The oxidation of some organic compounds is accompanied by undesirable side reactions of hydrolysis, substitution and and addition caused by the action of water and bromine ions.
3. In some cases the reactions of potassium bromate with organic substances are not strictly stoichiometric. This leads to a distortion of the final analytical results.

Nitritometry

Nitritometry, or nitrite titration, is a method of quantitative determination of substances using a titrant $NaNO_2$ sodium nitrite solution.

The method is based on the use of an acidic reaction medium.

$$NO_2^- + \tilde{e} + 2H^+ \longrightarrow NO + H_2O$$

The method is based on

- ✓ oxidation-reduction reactions,
- ✓ diazotization,
- ✓ nitrosation,
- ✓ azation.

Nitritometry

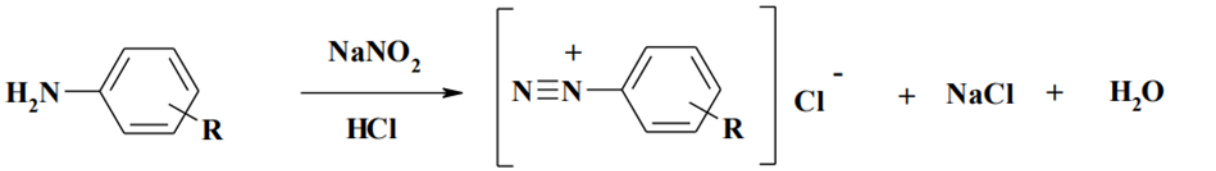
As an ***oxidising agent***, sodium nitrite is used for the determination of the reducing agents tin Sn^{2+}, iron Fe^{2+}, hydrazine and other compounds. At the same time the nitrite is reduced to nitric oxide:

$$HNO_2 + H^+ + \bar{e} \leftrightarrow NO + H_2O$$

As a ***reducing agent***, sodium nitrite is used for the determination of potassium permanganate, chlorine, potassium iodate and other compounds by reaction:

$$HNO_2 + H_2O - 2\bar{e} \leftrightarrow NO_3^- + 3H^+$$

The most often used reaction is ***diazotation***, which takes place with primary aromatic amines in an acidic medium:



Nitritometry

Preparation of the working solution and its standardization

The method **titrant sodium nitrite** ($NaNO_2$) is usually used as an aqueous solution with a concentration of 0.1 or 0.5 M.

The solution is prepared in an approximate concentration as sodium nitrite is unstable during storage and can oxidise to nitrate.

Standardisation of sodium nitrite is carried out according to the reaction that to be used for the determination.

If $NaNO_2$ is used

- as an oxidizing agent, it is standardized for iron(II), arsenic(III), hydrazine,
- as a reducing agent, it is standardized for potassium permanganate (secondary standard), potassium dichromate,
- in diazotization reactions, it is standardized for sulphanilic acid, p-minobenzoic acid, p-

Nitritometry

Fixing the titration end point

Instrumental method. The end of the titration in nitrite titration is most often recorded electrometrically by a potentiometric titration.

Indicators

Internal indicators

tropeolin 00 (colour change from red to yellow)

methylene blue (colour change from crimson to blue)

neutral red (colour change from red-purple to blue)

Nitritometry

Fixing the titration end point

Indicators

External indicators.

Starch-iodide paper is commonly used as an external indicator. It is a filter paper soaked in starch and potassium iodide solution and then dried.

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

The iodine produced in the presence of starch turns the paper blue.

Nitritometry

Conditions for nitritometric titration

1. Titration is carried out in an acidic medium (usually HCl).
2. It is necessary to work at 15–20 °C (in some cases with cooling down to 0–5 °C). Because at higher temperatures the resulting reaction products (diazonium salts) may be destroyed, and at lower temperatures the interaction speed of the titrant with the substance to be determined may decrease.
3. The titrant must be added slowly because the reaction goes through several intermediate stages.
4. KBr catalyst is used to speed up the reaction.

Nitritometry

Applications in pharmaceutical analysis

Inorganic substances

- tin(II), arsenic (III), iron (II), hydrazine and its derivatives

Organic compounds containing

- a primary or secondary aromatic amino group
- aromatic nitro derivatives (after prior reduction of the nitro group to an amino group), and hydrazides

Nitritometry

Applications in pharmaceutical analysis

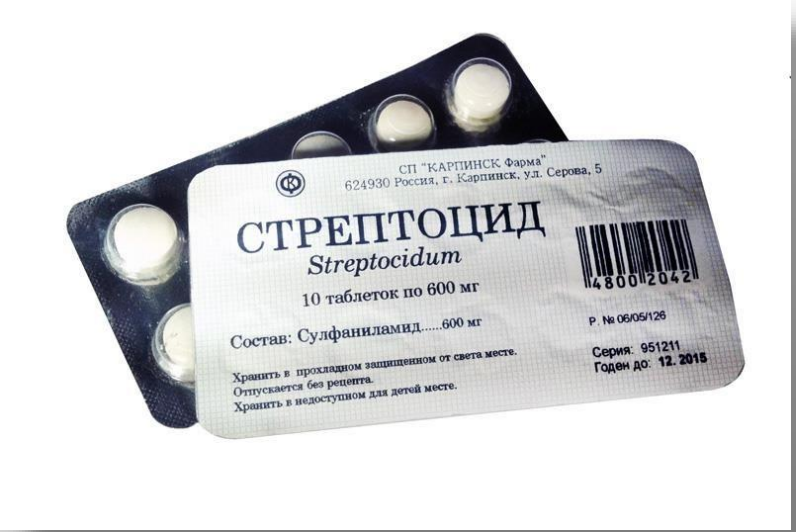
Iron (II) salts
Titrant NaNO2

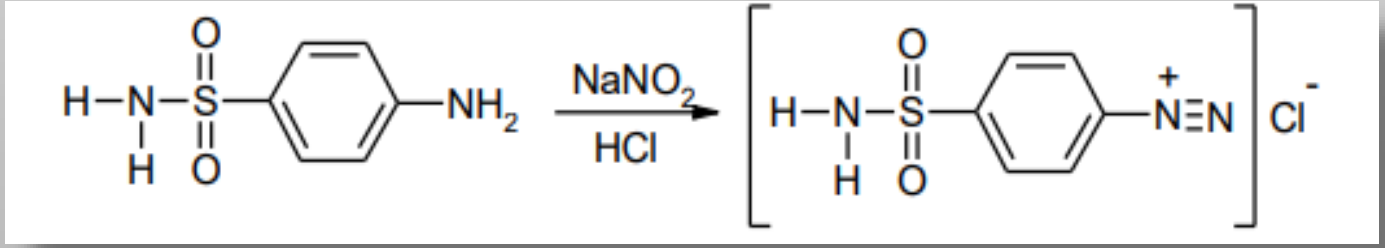
$$Fe^{2+} + NO_2^- + 2H^+ = Fe^{3+} + NO + H_2O$$

Nitritometry

Applications in pharmaceutical analysis

Sulphonamide
Titrant $NaNO_2$
Indicator tropeolin 00

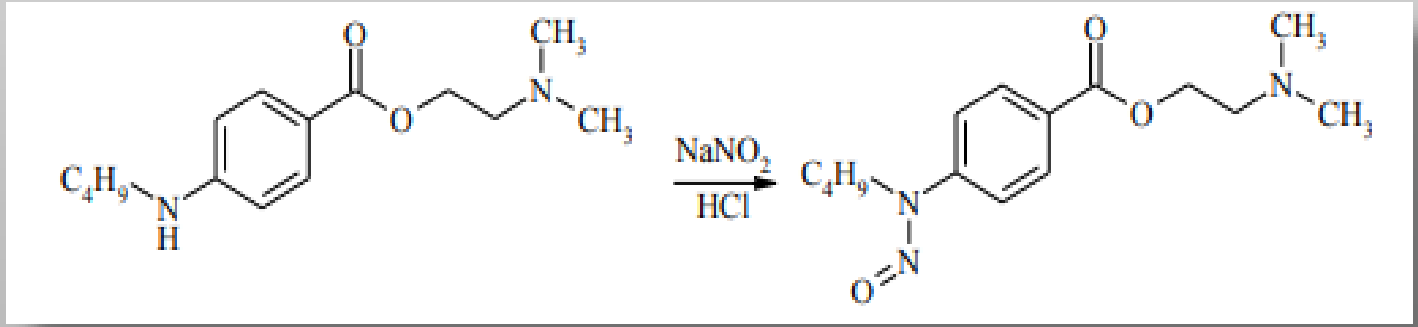




Nitritometry

Applications in pharmaceutical analysis

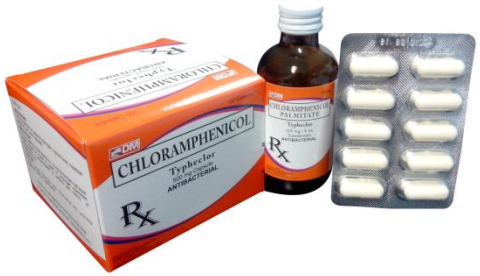
Tetracaine
Titrant $NaNO_2$
Indicator tropeolin 00

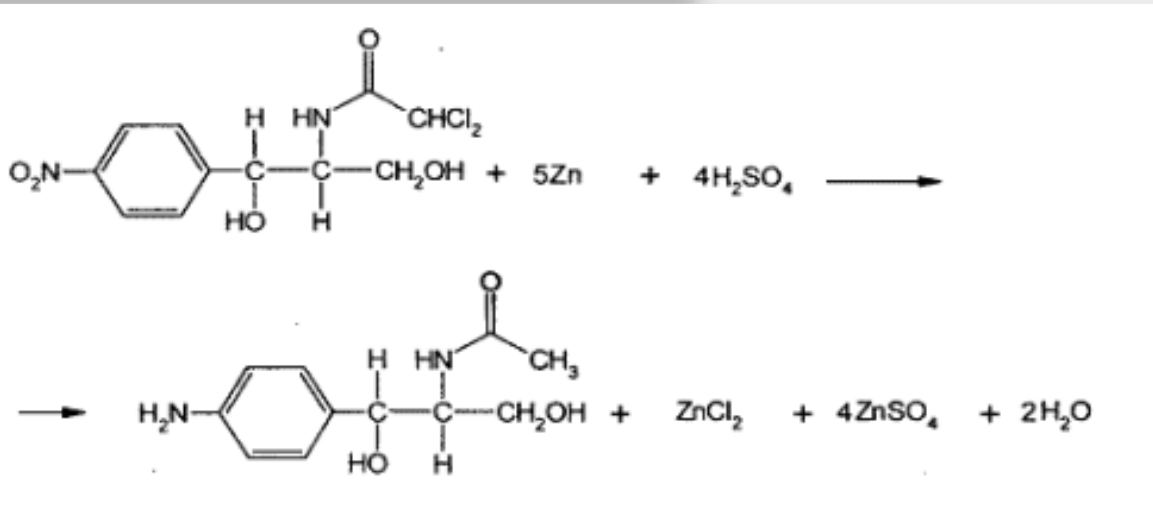


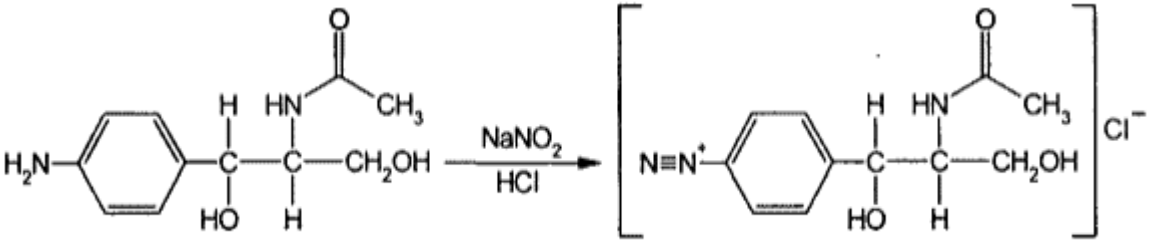
Nitritometry

Applications in pharmaceutical analysis

Chloramphenicol
Titrant $NaNO_2$
Indicator tropeolin 00







Thank you for attention!