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ION-PAIR EXTRACTION-TITRATION OF INORGANIC IONS WITH ONE PHASE END-POINT CHANGE SYSTEM. DETERMINATION OF COPPER AND PERCHLORATE ION

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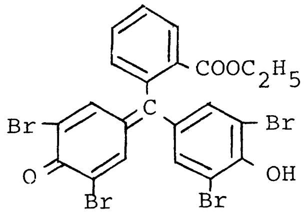
A new titration method is proposed for the determination of inorganic ions such as copper(I) and perchlorate ion. It is based on the solvent extraction-titration with the change of indicator in only one phase without movement of the indicator from one phase to the other. Tetrabromophenolphthalein ethyl ester and 2,6-dichlorophenolindophenol are used as the indicator.

Various reports have appeared regarding the solvent extraction-titration method. Wang and Panzardi published a general survey and background of solvent extraction-titration and described a modified two-phase titration using Azure A and Methyl Orange as the primary and secondary dyes respectively.1) The most methods regarding the extraction-titration are of the dye transfer type with color changes transferring from one phase to a second phase during the titrations. And none of the inorganic ions could not be determined by the dye transfer method.

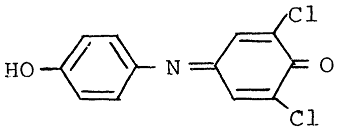
The authors recently developed a new extraction-titration method for the determination of berberine,2) where a two-phase system was used except the indicator dye color changes are all in one phase. This one phase end-point change system provided the solvent extraction-titration methods for the determination of inorganic ions such as copper(I) and perchlorate ion.

The recommended procedures are as follows: —— Copper(I) —— 2 ml of ascorbic acid solution (5%), 1 ml of pyridine, 1 - 10 ml of copper(II) sulfate solution (0.002 M), 5 ml of phosphate (0.3 M) - borate (0.05 M) buffer solution (pH 7 - 9.5), 2 - 3 drops of tetrabromophenolphthalein ethyl ester potassium salt solution (0.1% in ethanol), and 10 ml of 1,2-dichloroethane were placed in a 200-ml Erlenmeyer flask. The mixture was titrated with 0.002 M sodium tetraphenylborate solution with intermittent shaking by hand to ensure equilibrium between the organic solvent and aqueous phase. The 1,2-dichloroethane phase was sky blue. When one drop of excess tetraphenylborate solution was added, the organic phase changed to a yellow color indicating the end-point of the titration.

Perchlorate ion —— 1 - 10 ml of sodium perchlorate (0.01 M), 5 ml of phosphate buffer solution (0.3 M, pH 6 - 7), 3 - 4 drops of 2,6-dichlorophenolindophenol sodium salt solution (0.1% in ethanol), and 10 ml of nitroethane were placed in a 200-ml Erlenmeyer flask. The mixture was titrated with 0.01 M tetraphenylphosphonium chloride solution in the same manner as for the titration of copper(I). The nitroethane phase was pink. When one drop of excess titrant was added, the organic phase changed to a blue color indicating the end-point of the titration. The aqueous layer remains colorless throughout the titration, due to the water insolubility or hydrophobic property of these indicators as:



tetrabromophenolphthalein ethyl ester



2,6-dichlorophenolindophenol

The basic reaction for the titration can be represented by:

$$[\text{Cu(I)-pyridine complex}]^+_{aq} + [\text{TPB}]^-_{aq} \longrightarrow ([\text{Cu(I)-pyridine complex}]^+\cdot[\text{TPB}]^-)_{org}$$

$$[\text{ClO}_4]^-_{aq} + [\text{TPP}]^+_{aq} \longrightarrow ([\text{TPP}]^+\cdot[\text{ClO}_4]^-)_{org}$$

The end-points of the titration are described by the following equations:

$$\underset{\text{blue}}{([\text{Cu(I)-pyridine complex}]^+\cdot[\text{TBPE}]^-)_{org}} + [\text{TPB}]^-_{aq} \longrightarrow ([\text{Cu(I)-pyridine complex}]^+,[\text{TPB}]^-)_{org} + \underset{\text{yellow}}{[\text{TBPE}]_{org}}$$

$$\underset{\text{pink}}{[\text{DCP}]_{org}} + [\text{TPP}]^+_{aq} \longrightarrow \underset{\text{blue}}{([\text{TPP}]^+\cdot[\text{DCP}]^-)_{org}}$$

where org is the organic phase, aq is the aqueous phase, TPB is tetraphenylborate, TPP is tetraphenylphosphonium, $[\text{TBPE}]^-$ is the dissociated tetrabromophenolphthalein ethyl ester, and [DCP] is the nondissociated 2,6-dichlorophenolindophenol.

The hydrophobic ions such as anionic and cationic surfactant interfere the determination.

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References

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