DETERMINATION OF MICROMOLAR CONCENTRATION OF OXIDIZERS-DIZINFECTANTS WITH AQUEOUS MICELLAR HEXADECYLPYRIDINIUM CHLORIDE AND HEXADECYLTRIMETHYLAMMONIUM BROMIDE

Blazheyevskiy M. Ye., Riabko D. N.)*

***Pharmaceutical Corporation "ARTERIUM", Kiev**

Pharmaceutical National University, Kharkiv

Most of the methods used in the quantitative determination of oxidizers in the micromolar concentration range use solvent extraction of iodine complexes. As alternative to solvent extraction for the quantitative determination of sparingly water soluble compounds micelles have been used. Micelles can be used not only for solubilization but also for increasing the sensitive and/ or selectivity of analytical methods. The use of micellar hexadecylpyridinum chloride (cetylpyridinum chloride; CPC) and hexadecyltrimethylammonium bromide (CTAB) as a convenient medium for the quantitative determination of oxidant - disinfectants in the micromolar range by spectrophotometry is described.

The proposed method is based on the reduction of oxidizers-disinfectants by iodide in cationic micellar medium provided by CPC. In addition, the effect of CPC on the spectra of iodine-containing solution is analyzed in terms of the distribution of iodine and iodide between water and the micellar pseudo-phase. Iodine solubilization in micelles, and iodine ion binding to micellar CPC, should result in an increase of the local concentration of both reagents in the micellar pseudo-phase producing an increase in the apparent equilibrium constant for the formation of I_3^-. The association between triiodide ion and CPC micelles is discussed. The formation of the I3--CPC system under given conditions results in a bathochromic shift from 350 nm (adsorption wavelength of the I3- complex, ε=2,4·104) to 500 nm (maximum adsorption wavelength of the I3--CPC association) in addition to a substantial increase in the absorptivity and stability constant of the triiodide complex. This effect allows to increase of the sensitivity and/ or selectivity of the photometric procedure.

$$KHSO_5 + 2KI + H_2SO_4 = I_2 + H_2O + KHSO_4 + K_2SO_4$$

$$I_2 + 2KI = KI_3$$

Under the optimal conditions (3·10–5 mol·L-1 CPC, 2·10–4 mol·L-1 KI, pH 4-9 NaH_2PO_4+$NaHPO_4$) established, the molar absorptivity of the I3--CPC association was found to be 5,4·104 (i.e., ~2,3 times than in water). The standard error of the estimate was 5·10–3 absorbance units (n=7). LOD (3σ) was 1,4·10–7 mol·L-1. For example, the RSD was 2,3% (n=10) for 155 ng·mL-1 $KHSO_5$.

Also the influence of CTAB to the adsorption properties of water solutions, containing iodine and potassium iodide and allocating of iodine and triiodide between water and micellar pseudo-phase has been investigated. Injection of CTAB leads to increasing of analytical concentration of triiodide-ions and increasing of absorption in 290 nm (ε=3,8·104) and 360 nm (ε=1,6·104). Because of solubilization of iodine into micelles and bounding of iodide ions with micelles the increasing of iodine concentration and iodide-ions in the micellar pseudo-phase has been observed. Analytical concentration of triiodide-ions mostly depends on concentration of CTAB and Sodium bromide. Because of that the direct determination of iodine is possible only at the presence of strictly controlled medium ionic composition, concentration of CTAB and iodide-ions. The optical dense in 290 nm and 360 nm is proportional to the micromolar concentration of oxidants in the range 5·10-7 - 5·10-5 mol·L-1 (l= 3 cm) in solutions containing 4·10-3 mol·L-1 of CTAB and 1,8·10-4 mol·L-1 of potassium iodide. The chemical transformations, taken as a basis of analytical methods, for example of H2O2, are shown on the scheme:

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O + H_2O + H_2O_2 = (NH_4)_6Mo_7O_{25} + 5H_2O$$

$$(NH_4)_6Mo_7O_{25} + 2J^- + 2H^+ + J_2 + H_2O.$$