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SALTING-OUT EFFECT IN SOLVENT EXTRACTION(I) SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH 2-THENOYLTRIFLUOROACETONE

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A new solvent extraction technique using salting-out effect is described and shown to be applicable to the rapid and selective determination of iron(III).

The proposed method of solvent extraction is based on the following process: A metal complex is formed in a homogeneous solution composed of 2-propanol and water (1:1,v/v), and then the solution is separated into two phases by adding a salting-out agent. During the above process the metal complex is extracted into 2-propanol phase. Although this process seemed to have a resemblance in principle to the method developed by MURATA and IKEDA[1] in which a homogeneous solution should be formed at higher temperature above 70°C, according to the present method, all processes for the extraction are carried out at room temperature and the metal complex with slow formation rate can be extracted rapidly. The present method also gives an additional advantage that a water soluble organic reagent may be employed for color development in the organic phase without any process such as back-extraction.

At first, the above mentioned procedure is applied to the separation and determination of iron(III) with 2-thenoyltrifluoroacetone(TTA=Htta).

Take a sample solution containing up to 160 μg of iron(III) in a separatory funnel and add 1 ml of 0.5 N nitric acid. Adjust the volume of the solution to 10 ml with deionized water. Add 10.0 ml of 0.10 M TTA-2-propanol solution and shake the mixture gently. Then separate the homogeneous solution into two phases by dissolving 4.5 g of sodium nitrate, and measure the absorbance of the organic phase at 510 nm. The final volume of 2-propanol phase was found to increase to 12 ml after phase separation.

Average absorbance of ten runs taking 100 μg of iron(III) was obtained to be 0.610 ± 0.006, the sensitivity being 0.014 μg Fe/cm^2 at 510 nm, which is slightly lower than those reported by earlier workers[2,3]. Since the extractability of iron(III) was confirmed to be 98.4 % by single extraction, the lower absorptivity is attributable to the composition of the TTA complex in the present extraction, as is described later. A quantitative extraction of iron(III) using 10.0 ml of 0.10 M TTA-2-propanol solution can be attained over the nitric acid concentration range 0.0015 N to 0.10 N. An increase in absorbance exceeding 0.610 at the TTA concentration above 0.15 M was observed, which is probably due to the formation of $Fe(tta)_3$.

According to the previously reported extraction system, the extraction rate of the iron(III)-TTA complex is known to be extremely slow and the rate-determining step is assigned to the formation of the first TTA complex[4]. In order to estimate the composition of the extracted TTA complex in 2-propanol phase, the continuous variation method was applied. Keeping the total concentration of TTA and iron(III) constant (9.0×10^{-4}M), molar ratio of TTA to iron(III) in a homogeneous solution was varied. After the addition of 4.5 g sodium nitrate, the solution was shaken for 90 minutes. As a result, the maximum absorbance was observed at a molar ratio of TTA to iron(III) = 2:1, indicating that the extracted TTA complex contains $Fe(tta)_2^+$ in its composition. Since the TTA complex extracted in 2-propanol phase by employing the recommended procedure could not be transferred into benzene, the main complex in 2-propanol phase may be some charged species other than $Fe(tta)_3$. Another experiment was also tried: Homogeneous solutions with the same condition as above were prepared. Then the equilibrium for the formation of iron(III)-TTA complex was attained by standing each solution for 16 hours at room temperature, then 2-propanol phase was separated from the homogeneous phase. The resulting absorbance of 2-propanol phase was found to increase with the standing time and finally reach a constant value after 15 minutes. Since only $Fe(tta)^{2+}$ is expected to exist in homogeneous solution in which the molar ratio of TTA to iron(III) is lower than unity[5], the above increase in the absorbance is attributable to the formation of $Fe(tta)_2^+$ in 2-propanol phase after the phase separation. The preferential extraction of the first TTA complex of iron(III), which has been emphasized as an advantage of the homogeneous liquid-liquid extraction method by MURATA, YOKOYAMA and IKEDA[6], can also be performed at room temperature by the present technique. The presence of considerable amounts of nitrate in 2-propanol phase strongly suggests that the main complex may be $Fe(tta)_2NO_3$, whose absorptivity is expected to be lower than that of $Fe(tta)_3$. In addition, the formation of $Fe(tta)_2^+$ under the conditions of the recommended procedure was confirmed to complete within one minute.

Effect of diverse ions on the determination was also examined: Ten mg each of Ag, Al, Ca, Co(II), Cr(III), Hg(II), Mn(II), Pb, Sr, Th, Tl(I) and Zn, 100 μg each of Bi, Mo(VI) and Ni, and 10 μg of Cu(II) and V(V) gave no interference with the determination. However the extractability of iron(III) was lowered by the addition of phosphate, tartrate and citrate ion respectively, among which the last one was found to form a reddish mixed ligand complex of iron(III)-TTA-citrate system. The results show that the present extraction technique is applicable to the extractive spectrophotometric determination as well as the rapid separation of metal ion.

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