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Two sensitive extraction-spectrophotometric methods for determination of vanadium in catalysts of conversion of sulfur dioxide to sulfur trioxide have been developed. They are based on the ternary ion-association complexes of vanadium(V) with azoderivatives of resorcinol {4-(2-pyridylazo)-resorcinol (PAR), 4-(2-thiazolylazo)-resorcinol (TAR)} on the one hand and tetrazolium salts {tetrazol violet (TV), triphenyltetrazolium chloride (TTC)} on the other hand, respectively. The limit of direct application of the methods has been outlined - iron to vanadium ratio in the sample 0.4 to 1. The proposed methods were applied to analyse used Monsanto LP - 110 and LP-120 catalysts and good results were obtained in terms of precision and accuracy.