

**DETECTION OF CENTRAL ATOMS OF KEGGIN TYPE  
POLYOXOMETALLATES WITH LUMINOL BY MEANS OF HETEROGENEOUS  
CHEMILUMINESCENCE**

*Zuy O.V.*, Mazna Yu.I.

Dumansky Institute of Colloid and Water Chemistry  
of the National Academy of Sciences of Ukraine, Kyiv, Ukraine  
olegzuy@gmail.com

Heterogeneous chemiluminescence (CL) was used to determine ultramicroconcentrations of phosphorus, silicon, germanium in the form of polyoxometallates (POMs) [1]. The sorption of non-reduced POMs of phosphorus, silicon, germanium on cellulose filters of various nature (cellulose and diethylaminoethylcellulose), including paper filter, is quantitatively characterized [2]. Experiments on sorption have shown that the POM capacity of DEAE-cellulose is approximately 20 times higher than that of native cellulose. At the same time, the use of modified cellulose does not lead to a significant decrease in the detection limit of phosphorus by sorption of POM with CL detection of sorbate on the surface. The detection limit of POM on the surface of modified cellulose decreases only 1.7 times. This is due to the relatively high signal of the blank experiment when using modified cellulose compared to unmodified cellulose, which is explained by the more efficient sorption of isopolymolybdate ions on DEAE-cellulose. Unmodified cellulose has a lower affinity for isopolymolybdate due to the absence of diethylaminoethyl groups, and the nonspecific sorption of anions on it is lower. Therefore, the selectivity of the interaction of the sorbent with POM in conditions of excess of isopolymolybdate ions in aqueous solution is higher in the case of native cellulose.

The sorption equilibrium on DEAE-cellulose is established for a longer time than on unmodified cellulose, which is explained by the complication of the conditions for diffusion of POM anions into the pores of the modified cellulose. According to the Giles classification, the sorption isotherms of POM are classified as L-type isotherms. L-type isotherms are observed when the interaction between adsorbed molecules is very weak. They indicate a significant affinity of the sorbent for sorbate. In this case, the extraction of POM into the cellulose phase occurs due to anion exchange.

In the electronic spectra of cellulose and DEAE-cellulose samples upon immobilization of molybdovanadophosphate acid on the sorbent, a bathochromic shift is observed in the spectrum of its absorption band as compared to the aqueous solution. This band is stipulated by charge transfer between the oxygen atom and the Mo(VI) atom in the adsorbed POM anion. The change in the charge transfer energy of POM in the phases of cellulose and DEAE-cellulose indicates a change in the energy of molecular orbitals of the heteropolymetallate, which indicates a strong electrostatic interaction between the heteropoly anion and the polymer matrix.

It has been shown that  $^{31}\text{P}$  signal in the NMR spectrum of sorbed POM is broadened compared to the signal of crystalline POM, which is associated with the removal of crystalline and structural water. The broadening of the  $^{31}\text{P}$  NMR peaks of the immobilized POM is also due to a change in the symmetry of this POM as compared to the symmetry of the POM in the crystalline form. In turn, it is caused by a strong electrostatic and hydrophobic interaction

between the POM and the sorbent. Thus, based on the evolution of the NMR spectra, it can be assumed that there is a partially dehydrated POM on the surface of the sorbent, bonded electrostatically and due to hydrophobic interaction with the cellulose surface.

The mechanism of sorption lies in a combination of Coulomb and hydrophobic interactions. As hydrophobic interactions are characterized by low energy (41.9 kJ/mol), hydrogen bonds ~41.9, and ionic reach ~419 kJ/mol, it is evident that at pH 1.0–1.7 the determining factor for the sorption of POM anions is the Coulomb interaction. The theoretical basis for the use of heterogeneous chemiluminescence in the determination of phosphate, silicate, germanate is the derivatization of oxoanions with the formation of chemiluminescence-active analytical forms – polyoxometallates, which are sorbed and separated on a solid sorbent and instantly react with luminol on the sorbent surface. The proposed analytical forms are characterized by sufficient sorption capacity, which ensures their separation from the matrix and interfering contaminants.

Chemiluminescent reactions with luminol of polyoxometallates  $H_4PVMo_{11}O_{40}$ ,  $H_4AsVMo_{11}O_{40}$ ,  $H_4SiMo_{12}O_{40}$ ,  $H_5GeVMo_{11}O_{40}$  in aqueous solutions, as well as after immobilization on cellulose and DEAE-cellulose filters, have been studied [3]. A scheme of CL reactions was proposed, including catalytic oxidation of the luminol anion to the semiquinone radical by atmospheric oxygen through the POM redox cycle, oxidation of the semiquinone radical with oxygen to form diazaquinone and superoxide radical anion, oxidation of the semiquinone radical by superoxide to luminol peroxide, which further decomposes to aminophthalate with light emission. Carrying out reactions with luminol solution directly on the surface of the sorbent makes it possible to achieve high sensitivity for the determination of Phosphorus, Germanium, Silicon due to preconcentration of POM during sample filtration.

The CL method was used to establish conditions of interaction of POMs of arsenic, phosphorus, silicon, germanium with long-chain ammonium or pyridinium bases [4]. It is shown that ionic associates (IA) are formed, which are quantitatively separated on a paper filter during filtration of aqueous solutions and are detected directly on the sorbent surface by CL method. When filtering solutions containing IA, a mixed retention mechanism on filters is implemented, based on the physical retention of water-insoluble IA, as well as on the hydrophobic interaction of electroneutral IA with the sorbent surface.

The composition of poorly soluble IA of the listed POMs with long-chain cationic surfactants (dodecylpyridinium bromide DDPB, tetradecylpyridinium bromide TDPB, cetyltrimethylammonium bromide CTB) was investigated by Bjerrum's method, by equilibrium shift method and by molar ratio method after filtration through cellulose filters using CL reactions of isolated IA with luminol. Integral light amount and maximum light intensity were used as characteristics of the system.

The composition of IA POM-surfactant is determined:  $(CT)_4SiMo_{12}O_{40}$ ;  $(CT)_5GeVMo_{11}O_{40}$ ;  $(TDP)_4AsVMo_{11}O_{40}$ ; in the case of molybdovanadophosphoric acid, the composition of IA is different at different pH: at pH 1.0, the composition of IA is  $(DDP)_3H[PVMo_{11}O_{40}]$ ; at pH 1.7 –  $(DDP)_4[PVMo_{11}O_{40}]$ . This result is consistent with the data that the fourth proton in  $H_4PVMo_{11}O_{40}$  is weakly dissociated; it is more strongly bound to POM and is localized on the oxygen atom of the Mo – O – Mo angular bond. Thus, as a

result of protonation of POM upon going from pH 1.7 to pH 1.0, the acid  $H_4PVMO_{11}O_{40}$  forms not tetra-substituted, but triply substituted IA.

IAs POM-cationic surfactant react with an alkaline solution of luminol with light emission similarly to POMs themselves. Their isolation on cellulose filters and detection by CL method directly on the sorbent surface made it possible to improve substantially the sensitivity of the determination of Phosphorus, Arsenic, Silicon, and Germanium.

Due to the high sensitivity of the method Phosphorus was successfully determined in surface water and in ultrapure water, Arsenic after distillation in the form of volatile  $AsH_3$  – in river and mineral water, Silicon – in ultrapure water and vapor condensate of electric power stations, Germanium – in highly pure water of electronic industry.

#### References:

1. Zui O.V. Heterogeneous chemiluminescent assay // *Inorganic Materials*. – 2010. – Vol. 46, No. 14. – P. 1518-1525.
2. Zui O.V., Zaitsev V.N., Alekseev S.A., Trachevsky V.V. Sorption of heteropoly acids on cellulose sorbents // *Chemistry, Physics and Technology of Surface*. – 2012. – Vol. 3, No. 1. – P. 66-73.
3. Zui O., Takahashi H., Hori T., Hinoue T. Luminol chemiluminescence under interaction with heteropoly acids // *Talanta*. – 2009. – Vol. 78, No. 3. – P. 1185-1189.
4. Zui O.V. Application of chemiluminescence for the determination of composition of ion associates of heteropoly acids with cationic surfactants. – *Methods and Objects of Chemical Analysis*. – 2011. – Vol. 6, No. 1. – P. 51-57.