PECULIARITIES OF CATALYTIC REACTION OF LUMINOL OXIDATION BY OXYGEN IN PRESENCE OF TRANSITION METALS AND ITS APPLICATION FOR THE DETERMINATION OF COBALT TRACES IN NATURAL WATERS

Mazna Yu.I., _Zuy O.V._

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

Cobalt is a natural earth element and is present in trace amounts in air, soil, water, plants and in food. It is used in alloys, as catalyst for petroleum and chemical industries. Cobalt is beneficial for humans because it is a part of vitamin B_{12}, which is essential for human health. Too high concentrations of cobalt may damage human health. Intake of excess cobalt may lead to interstitial lung disease and cardiomyopathy in humans and animals [1]. Since one of the routes of incorporation of cobalt into the human body is by ingestion, its determination in food and drinking water is very important. Cobalt concentrations are very low in water samples, and therefore, simple and sensitive analytical techniques are required to make its detection possible.

One of the most sensitive techniques for trace metal determination is ICP-MS spectrometry but it is rather costly and requires complicated equipment. A promising method for this purpose is chemiluminescence method being cheap, highly sensitive and rapid one [2].

A number of transition metals catalyze the reaction of luminol with hydrogen peroxide. Some of them also catalyze the reaction of luminol with oxygen [3], the most efficient catalyst is Co(II). However procedure for cobalt determination in natural waters via chemiluminescence in the system mentioned is not known. We examined the peculiarities of catalysis of the reaction of luminol with oxygen dissolved in water by transition metals on the example of cobalt(II).

In the present work traces of cobalt were determined by using the chemiluminescence appearing on mixing of alkaline solution of luminol and neutral solution of Co(II) salt without specially added oxidants or other reagents. The decrease in the intensity of the chemiluminescence on passage of argon through the solution shows that oxygen participates in the reaction. In the luminol – Co(II) – O_2 system it is possible to suggest formation of free oxygen radicals oxidizing luminol with light emission, since cobalt complexes are known which reversibly absorb and activate oxygen. Cobalt complexes containing a superoxide bridging ion are active in reaction with luminol while complexes without superoxide are generally inactive [4]. In the luminol – O_2 reaction solutions of Co(II) salts at pH $\geq$ 8 are inactive.

The optimal conditions were established for the chemiluminescent reaction of luminol with cobalt and oxygen, and the effect of a number of complex forming agents as well as of macro- and microcomponents of surface waters was studied.

The reaction in the luminol – Co(II) – O_2 system is accompanied by a flash-like light emission, the intensity and duration of which depends on pH, concentration of reaction

components, and mixing order (MO) of the solutions. The most intense light emission is observed at pH 12.0 – 12.5 and MO of (luminol, NaOH) + Co(II); at MO luminol + (Co(II), NaOH) weak light emission is observed due to rapid deactivation of the catalyst on addition of alkali. The shape of the kinetic curves of chemiluminescence changes depending on the luminol concentration, with most prolonged light emission at luminol concentration $5 \times 10^{-5} - 2 \times 10^{-4}$ M, a further increase in the luminol concentration causes an increase in the intensity of the initial peak and a decrease in chemiluminescence duration. At the concentration of luminol equal to 1×10^{-3} M the lowest limit of detection of Co(II) is achieved. Under the optimal reaction conditions of pH 12.5, luminol concentration 1×10^{-3} M, MO (luminol, NaOH) + Co(II), a linear relationship is observed between the maximum intensity of light emission and the cobalt concentration in the range $1.5 \times 10^{-10} - 5 \times 10^{-7}$ M; the blank light emission, i.e. light emission of alkaline luminol under the effect of atmospheric oxygen, is low and stable. The cobalt detection limit is 0.01 µg/L by the 3σ–criterion. The relative standard deviation of cobalt determination does not exceed 0.07 (n = 5, P = 0.95).

In order to stabilize the active form of the catalyst in the reaction of oxidation of luminol by atmospheric oxygen the effect was checked of certain complexing agents on the intensity and duration of the light emission. These complexing agents were amines, amino acids, hydroxy acids, etc. They were chosen because some of them (hydroxyquinoline, triethanolamine) are activators of cobalt(II) in chemiluminescent reactions with H_2O_2; some form complexes with Co(II) in which the reaction Co(II) $\rightarrow$ Co(III) (ethylenediamine) proceeds rapidly under the action of atmospheric oxygen; some stabilize Co(II) in an alkaline medium in the presence of oxygen (glycine, glutamic, oxalic and citric acids). It was found that EDTA, NH$_4$OH, ethylenediamine, glycine, dimethylglyoxime, o-phenanthroline, diethylenetriamine, and triethanolamine inhibit the chemiluminescence reaction. Citric and glutamic acids increase the chemiluminescence intensity by a factor of 2-3, with no change in the duration of the light emission. None of the complexing agents tested permits to obtain a prolonged light emission in the luminol – Co(II) – O_2 reaction at luminol concentration 1×10^{-3} M.

The procedure for chemiluminescent determination of Co(II) in doubly distilled water is characterized by a low detection limit and is promising for analysis of natural waters. For its application in natural water analysis the effect of certain macro- and microcomponents of natural water on the intensity of chemiluminescence was investigated. It was found that Pb(II) and Zn(II) have no effect at a concentration of $\leq 1 \times 10^{-4}$ M; Ni(II), Cu(II) and Fe(III) inhibit the reaction at a concentration of $\geq 1 \times 10^{-6}$ M; SO_4^{2-}, Cl⁻, Br⁻, I⁻, NO_3^-, HCO_3^- do not affect the chemiluminescence intensity. Mg(II) and Ca(II) act as inhibitors of the chemiluminescent reaction at concentrations of $\geq 2.2 \times 10^{-5}$ and $\geq 5 \times 10^{-4}$ M, respectively. The inhibition observed is apparently related to coprecipitation of Co(II) at pH 12.5 with magnesium hydroxide and calcium carbonate. The effect of iron and magnesium is observed at concentrations in which these elements are present in natural waters. Some interfering components may be absorbed on Chelex-100 resin. In our samples of river and tap water the concentration of Ca(II), Mg(II), and Fe(III) was 50-65, 7-13, and 0.1-0.15 mg/L, respectively; in order to eliminate their interfering effect the water samples were diluted by a factor of 10. Some natural waters may contain elevated comcentrations of iron. When the concentration of Fe(III) was more than 3 mg/L it was bonded into inactive complex with sodium citrate or sodium salicylate. Sodium

citrate eliminates the inhibiting effect of Fe(III) and somewhat intensifies the activity of Co(II). The effect of sodium citrate in a mixture with Co(II) – Fe(III) is not additive as compared with the effect in the mixtures Co(II) – citrate and Fe(III) – citrate, which is apparently explained by the formation of heterometallic complexes. This effect is difficult to take into consideration if the concentration of iron in the samples varies.

The best complexing agent for Fe(III) under conditions of the chemiluminescent reaction is sodium salicylate at a concentration of $1 \times 10^{-3} - 1 \times 10^{-4}$ M which completely removes the interference of Fe(III) and does not increase the chemiluminescent signal of Co(II).

For decomposition of the organic contaminants, which also interfere with the determination, the water samples were treated with nitric acid and hydrogen peroxide.

Mineralization of the samples and addition of sodium salicylate to bond the iron leads to an increase in the intensity of blank light emission, as well as the necessity of predilution of the water samples by a factor of 10. These operations increase the detection limit of cobalt in water to 1.0 μg/L.

Samples of tap water and Dnipro river water (cobalt concentration in these samples was less than 1 μg/L) were spiked with Co(II) solutions to obtain cobalt concentrations of 2 μg/L in tap water, 5 and 25 μg/L – in river water, and then chemiluminescence determination of cobalt in water was carried out. The results obtained (2.1±0.6; 5.1±0.2; 25.2±0.2 μg/L respectively) correlate well with the results obtained by ICP-MS spectrometry. This proves that the procedure proposed may be used for trace cobalt determination in tap water and in river water.

References:
1. Abdolmohammad-Zadeh H, Ebrahimzadeh E. Determination of cobalt in water samples by atomic absorption spectrometry after preconcentration with a simple ionic liquid–based dispersive liquid–liquid micro-extraction methodology // Cent. Eur. J. Chem. – 2010. – Vol. 8, No. 3. – P. 617-625.
2. Chemiluminescence in analytical chemistry / Eds. A.M. Garsía-Campaña, W.R.G. Baeyens. – New York, Basel: Marcel Dekker, 2001. – 621 p.
3. Klopf L.L., Nieman T.A. Effect of iron(II), cobalt(II), copper(II), and manganese(II) on the chemiluminescence of luminol in the absence of hydrogen peroxide // Anal. Chem. – 1983. – Vol. 55, No. 7. – P. 1080-1083.
4. Pilipenko A.T., Zui O.V., Terletskaya A.V. A chemiluminescent method of determining cobalt in water by the catalytic reaction of oxidation of luminol by oxygen // Journal of Water Chemistry and Technology. – 1984. – Vol. 6, No. 4. – P. 48-53.