A SPECIFIC HIGHLY SENSITIVE FLUORESCENT REACTION FOR ALUMINUM

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Abstract

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A. I. CHERKESOV

A SPECIFIC HIGHLY SENSITIVE FLUORESCENT REACTION FOR ALUMINUM

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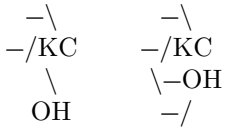
The most important organic reagents for aluminum are characterized by the presence of a hydroxyl group in the peri- or ortho-position to the atom forming the coordination bond. A large group of the reagents under consideration can be represented in the form of the following schemes ([1,2]):



Here KC is the atom forming the coordination bond with the aluminum ion.

Many oxyanthraquinones, which react with aluminum ions to form colored lakes or fluorescent reaction products, fit this scheme. Thus, a highly sensitive fluorescent reaction for aluminum with 1,4-dioxy-5,8-dichloroanthraquinone ([3]) was proposed; it proceeds on heating and in the presence of calcium carbonate. The authors characterize this reaction as specific, carried out in a sufficiently acidic medium; at higher pH values there can be no question of the specificity of the reaction under consideration, since in this case 1,4-dioxy-5,8-dichloroanthraquinone reacts with many other metal ions. The mechanism of this reaction has not been studied, and in this connection it is unknown to which type of reactions it belongs—to reactions of intracomplex formation or to the adsorption type.

Table 1

Comparison of the most sensitive fluorescent reactions for aluminum

Reagent	Minimum detectable, γ	Limiting dilution
Morin	0.005	$1:10^7$
1,4-Dioxy-5,8-dichloroanthraquinone	0.002	$1:10^6$
2,3-Oxynaphthoic acid	0.0002	$1:10^7$

The reaction mentioned, however, was the most sensitive of all fluorescent reactions for aluminum known up to the present time (Table 1).

In studying the analytical properties of certain aryl- and naphthylcarboxylic acids, we established that 2,3-oxynaphthoic acid I is a highly sensitive specific fluorescent reagent for aluminum.

2,3-oxynaphthoic acid	aluminum complex
Structure I	Structure II
$C_{10}H_6(OH)COOH$	$[C_{10}H_6(O)COO]_3Al$

2,3-Oxynaphthoic acid in aqueous solution at pH > 2 has a green fluorescence color in ultraviolet light; at pH < 2 it does not fluorescate; the color of the fluorescence in benzene is violet, in chloroform lilac, and in alcohol green; ether and carbon tetrachloride quench the fluorescence.

The vapors of 2,3-oxynaphthoic acid fluoresce violet, which makes it possible to suppose the presence, in aqueous solutions, of dimers of this compound arising as a result of the formation of hydrogen bonds; to them, evidently, the green color of the fluorescence should be attributed.

Fig. 1. Physical-chemical analysis of the system: Al^{3+}–oxynaphthoic acid (in solution). Along the abscissa axis are plotted the ratios of the volumes of the reacting components (molarity of the component solutions $1 \cdot 10^{-4}$).

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When 2,3-oxynaphthoic acid interacts with aluminum ions in an aqueous solution at pH 3 and above, a bright blue fluorescence appears, observed in ultraviolet light.

This reaction is carried out as follows. To 1 ml of a slightly acidic test solution, a saturated aqueous solution of the reagent is added dropwise; an excess of reagent should be avoided, since in that case the blue color of the reaction product may be masked by the green fluorescence of the reagent itself. The sensitivity of the fluorescent reaction corresponds to 0.01 γ of aluminum at a limiting dilution of $1 : 10^8$.

The reaction can also be performed by the drop method. For this purpose, filter paper is moistened with the reagent solution and dried. The reagent solution is prepared as follows: about 0.1 g of 2,3-oxynaphthoic acid and 0.2-0.3 g of urotropine are dissolved in 20 ml of water; if a residue of undissolved 2,3-oxynaphthoic acid remains, it is filtered off. The reagent paper fluoresces green in ultraviolet light; when moistened with water, the fluorescence color does not change.

To detect aluminum, a drop of the test solution is applied to the reagent paper; the solution may be fairly acidic (pH 2-3), and it is then subjected to ultraviolet irradiation. In the presence of aluminum, a blue fluorescence appears against the

green background. The sensitivity of the drop reaction is 0.0002 γ of aluminum at a limiting dilution of $1 : 10^7$.

The fluorescent drop reaction for aluminum with 2,3-oxynaphthoic acid is not interfered with by ions of the following elements (in their usual valence states): Ca, Sr, Ba, Mg, Zn, Cd, Hg, Pb, Sn, Ti, V, As, Sb, Bi, Cr, Mo, W, Mn, Co, Ni, Cu.

In the presence of ions Th^{4+}, UO_2^{2+}, and Fe^{3+}, as a rule, a nonfluorescent field is formed in the center of the spot: this is explained by the fact that thorium ions exert a strong quenching action, while UO_2^{2+} and Fe^{3+} ions form colored complexes with the reagent. However, owing to considerable radial capillary migration of the aluminum ions (capillary separation), a blue rim is always formed between the green fluorescence background of the reagent paper and the nonfluorescent dark spot. It should be noted that when the pH is lowered, the sensitivity of the reaction decreases. At high pH values (in the presence of free alkali), the detection of aluminum is interfered with by magnesium, which adsorbs the reagent on the surface of $Mg(OH)_2$ and gives an analogous fluorescence.

The supposition that the fluorescent reaction for aluminum with 2,3-oxynaphthoic acid is an adsorption reaction was not confirmed. First, this is contradicted by the existence of the reaction at pH values lower than the value at which appreciable hydrolysis of aluminum salts begins. Secondly, by the method of physical-chemical analysis[4,5], stoichiometric coefficients were determined, corresponding to—the reaction of intracomplex formation proceeds. In Fig. 1 the values of fluorescence intensity I are plotted on the ordinate axis.

It is seen from Fig. 1 that the fluorescence maximum occurs when the ratio of the volumes of equimolecular solutions of the components is equal to $1 : 3$ (at pH 5).

On the basis of the foregoing, it may be assumed that the composition of the intracomplex compound formed corresponds to the formula $(C_{11}H_8O_3)_3Al$, with the possible structure II.

Experiments observing the Tyndall effect established the colloidal state of the complex in solution.

The fluorescent reaction described may be used for the quantitative determination of traces of aluminum; moreover, work can be carried out with concentrations from 0.1 γ to 0.01 γ per 1 ml. It is recommended that quantitative determination of aluminum be performed by the standard-scale method, observed in ultraviolet light.

2,3-oxynaphthoic acid may also be recommended as a fluorescent indicator with a transition interval of 1.9–2.3 pH units.

Astrakhan Technical Institute
of the Fishing Industry and Economy

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Note: Figure translations are in progress. See original paper for figures.