

Green approaches to colorimetric monitoring of calcium in water*

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Abstract: Simple, ecologically harmless chemical reactions have always been a point of interest for chemists and analysts as fit to be applied to work in or out of laboratories. A new concept of chemical analysis is exemplified in the article by means of selective determination of calcium ions with the organic reagent arsenazo III (2,2'-[1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo]-bisbenzenearsonic acid disodium salt) with no application of toxic solvents during the seasonal analysis of water in the Yauza River (the city of Moscow).

Keywords: analytical chemistry; calcium determination; immobilized organic reagents; optical sensors; photogelatin film sorbent; rational nature management.

INTRODUCTION

Today it is essential to take into consideration the requirements of green chemistry while working out new analytical methods. In the book *Green Chemistry: Theory and Practice*, published in 1998, Paul Anastas and John Warner [1] present 12 major principles of green chemistry, some of which are applicable in modern analytical practice. For example, one can point out principle 1, which reads “Prevention: It is better to prevent waste than to treat or clean up waste after it has been created”, and principle 11 “Real-time analysis for pollution prevention: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances”. In this connection, great importance has been attached to new analytical methods that can be used for environmental monitoring in order to control the formation of hazardous substances. At the same time, it is desirable that methods excluding decomposition operations of the test sample by acids, evaporation with acids, extraction with toxic solvents, etc. be preferred. These methods are well achievable for most natural objects, especially water media. That is why hybrid analysis methods based on simultaneous concentration of elements and formation of the end product that can undergo immediate measurement have been widely practiced. One of these methods is the application of polymers of various types with immobilized organic reagents, which happen sometimes to be selective for the substances being determined [2–4]. One of the advantages of an analytical reaction proceeding in a polymer gel is its conformity with the principles of green chemistry. In this case, the application of biodegradable media for carrying out analytical reactions seems to be advantageous and is preferred, because the environmental safety of an analytical method is assigned to it in advance. For practical ap-

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plication, biodegradable materials that should combine a high level of technological and operating characteristics with the capability to biodegrade are of primary importance. Moreover, while using the “synthesis in gel” method, minimization of reagents and solvents consumption is achieved, which corresponds to the fundamentals of green analytical chemistry [5].

We have proposed homogeneous gels formed by hydrophilic polymers of different solubility. They have several analytical values such as optical transparency, a great number of reactive groups in a polymer macromolecule, which are suitable both for different variants of immobilization of organic reagents, preserving their analytical properties, and for modification of the polymer itself. The mentioned peculiarities of polymeric gels allow production of new sensitive materials [6] on their basis. These materials are fit to be used as probes as well as optical sensors by instrumental and/or visual indication. Thus, the “synthesis in gel” method can be implemented as one of the green chemistry methods in analytical practice. In this connection, one of the most prospective materials is gelatine gel, which represents an ampholytic ion exchanger (Fig. 1). Chemically purified gelatine (also known as photogelatine, which contains neither monomers nor hydrophobic inclusions such as touches of fat, dust, etc.) possesses a number of advantages such as uniformity of the deposited gelatine layer, proper buffer effect, a high sorption molecular capacity, a three-dimensional easily recoverable structure, low swelling ability due to the linear distribution on the support-film, matrix fractality, easy immobilization of reagents, quickness of interaction of metal ions with the immobilized organic reagent, and optical transparency. These peculiarities of the gelatine matrix have made it possible to work out sensitive methods of analysis based on the application of hardened gelatine gel for spectrophotometric (transmission and reflection) and test determination of a range of metals and anions on the basis of reactions that proceed in gels [2–4].

Optically transparent sensitive elements with immobilized forms of reagents have the advantage of expressibility and simplicity of detection over solutions as far as objectives of analytical chemistry are concerned, and in the sphere of environmental protection the advantage of these elements is environmentally friendly technology and easy utilization. Other advantages include mass and multielement character of the elements, possibility of visualization, and low costs of analysis. All this in total meets the requirements of green chemistry in the sphere of technology of chemical monitoring of environmental conditions and disease diagnostics. Chemical composition monitoring of natural waters provides information about the level of technological pollution of the environment in real time. One of the elements controlled is calcium as an integral part of hardness of water. Calcium is one of the microelements, its biological effect and geochemical role need to be investigated in detail and are viewed as extremely important when considering the issues of human health and vital functions in general. An increase in the content of calcium in natural water is a sign of a high degree of man-caused pollution. It is important to note that besides natural sources of calcium ions that enrich water reservoirs, the role of sewage of different plants and factories, farming, and other economic activity is constantly rising. That's why it is essential to develop new methods that meet the requirements of green chemistry and can be applied to determine calcium ions in natural waters [7,8].

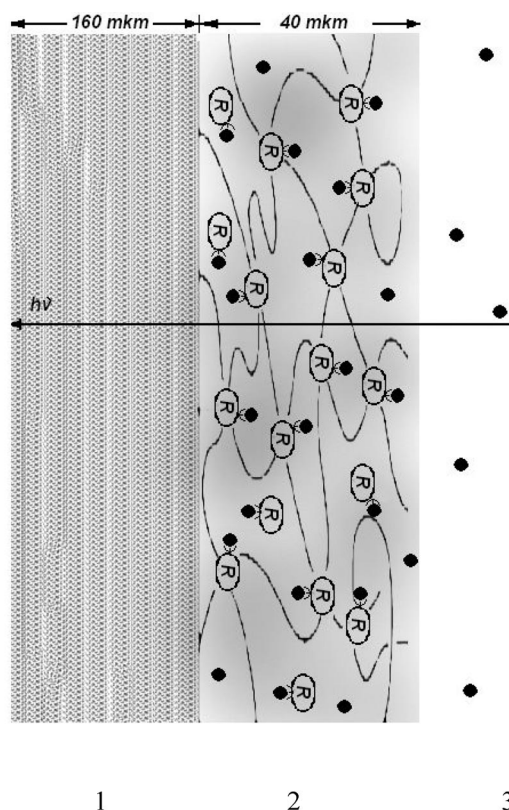
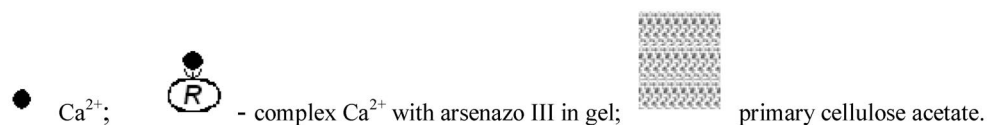


Fig. 1 Scheme of the layer structure of a polymeric material. Layers 1 and 2 constitute the carrier; solution – 3. The dimension of the carrier is 20×20 mm. The material is transparent, without organic reagents it has a yellowish tint.



SENSITIVE ELEMENTS BASED ON GELATINE GEL

We propose that the sensitive element (Fig. 1) based on gelatine gel with the electrostatically immobilized color-active reagent arsenazo III (**OR**) should be used in the environmental monitoring of the content of Ca^{2+} ions in the Yauza River within the precincts of Moscow during the spring flood. A sensitive element representing an optically transparent triacetylcellulose substrate covered with a layer of gelatine gel was used for spectrophotometric measurements. The organic reagent arsenazo III was chosen as color-active molecules for calcium ion detection.

Formation of the sensitive layer of the reagent, which is pink-colored, proceeds basically due to electrostatic interactions. The electrostatic mechanism of reagent immobilization into the gelatine medium was corroborated by specially conducted spectrophotometric research (Fig. 2). As the basic evidence of the statement cited above, we regard the fact that the maxima of absorption bands do not shift in the case of transplanting the analytical reaction from the water medium into that of gelatine gel. This sensitive element distinguishes itself through a high selectivity to calcium ions. The selectivity of the sensitive element to Mg^{2+} is provided by maintaining the $\text{pH} = 5\text{--}7$ (acetate buffer solution). In the process of quantitative spectrophotometric determination of calcium, maximal absorption correspon-

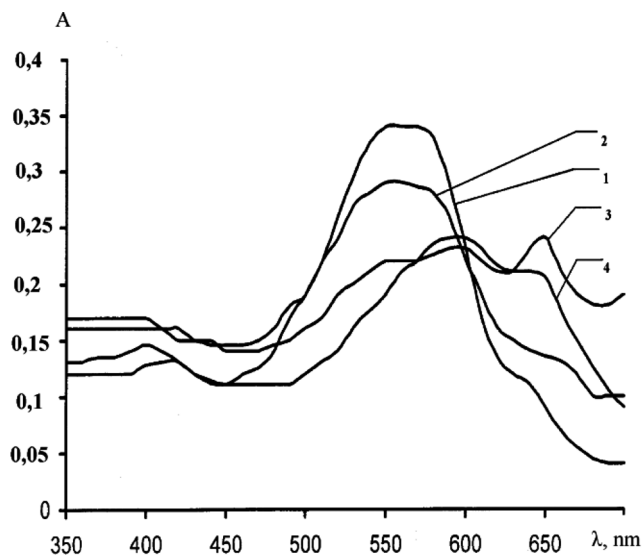


Fig. 2 Spectral characteristics of the system Ca^{2+} – arsenazo III: in water solutions (2, 4) and in gelatine gel (1, 3); static regime; $\ell = 0.2$ mm (1, 3) and 10 mm (2, 4); pH = 7; Concentration in the solution: $C_{\text{Ca}^{2+}} = 0.9$ M, $C_{\text{OR}} = 10^{-4}$ M. In relation to distilled water (2, 4) or in relation to the transparent gel layer on the substrate (1, 3); 1, 2 – R; 3, 4 – complex.

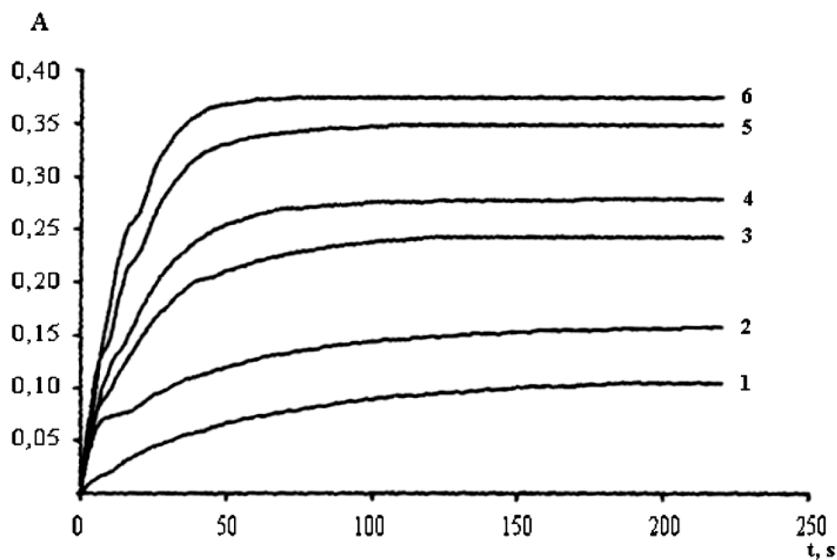


Fig. 3 Response of the sensitive element to Ca^{2+} with the immobilized arsenazo III. A digital spectrophotometer KFK 3-01 (Russia). pH = 7.7. Automatic measurement mode. Concentration of Ca^{2+} (mg/l): 1 – 21.64; 2 – 43.29; 3 – 86.57; 4 – 129.86; 5 – 175.15; 6 – 216.43.

ding to the saturation stretch on the kinetic curve (Fig. 3) was used as the analytical signal, the response time being equal to 2 min.

METHODS OF SPECTROPHOTOMETRIC MEASUREMENTS

A cell filled with a buffer solution with the pH = 6.8 was inserted into the spectrophotometer KFK-3-01 with digital registration of the signal, then a sensitive element with the immobilized arsenazo III was immersed in it and the device was set to optical zero. Then the solution under investigation (pH 6.8) containing Ca^{2+} was introduced into the cell and a certain intensification of absorption with time was registered. The data given in Fig. 3 display that during the time in which the reaction develops (about 1.5 min) the system runs up to the 95 % level of the signal from the maximum, the time of arriving at it is the response time. In the process of quantitative spectrophotometric determination of calcium, maximal absorption corresponding to the saturation stretch on the kinetic curve was used as the analytical signal, when the response time was assumed as equal to 2 min. The calibration dependence found in these conditions in the range of concentrations 5–320 mg Ca^{2+}/l is shaped as

$$A_{605 \text{ nm}} = (0.019 \pm 0.003) + (0.0013 \pm 0.0001) \cdot C_{\text{Ca}^{++}} \quad (1)$$

The correlation coefficient is $r = 0.99$, dispersion equals 0.02.

We should note that it is the wide range of contents that can be determined that makes the new sensitive element particularly useful for practical purposes.

TEST METHOD FOR VISUAL INDICATION (THE PROCEDURE OF ANALYSIS ACCOMPLISHMENT)

For visual testing, color scales for test determination of Ca^{2+} ion content were obtained. As a result of work aided by specially obtained color scales based upon tint transition from pink-lilac to clearly blue (a color step makes up 20 mg/l) quick semiquantitative determination of calcium in the range of concentrations between 10 and 200 mg/l in river water was accomplished. This test method consists in immersing a test agent into the analyzed water (five- to tenfold dilution with distilled water of the picked-out river water sample) for a period of 2 min. Then we went on to compare visually the test agent with the color scale.

As the main advantages of the proposed test agents, we can point out expressibility, low cost, easiness of production and determination accomplishment, the possibility of carrying out analyses in situ as well as the possibility of preserving analytical color information for a long period of time and determining the element afterwards with accuracy in the laboratory. Application of the sensitive elements in the form of a tape allows carrying out the analysis in flow cells in order to exercise control over technological solutions.

MONITORING OF Ca^{2+} CONTENT IN THE YAUZA RIVER (2007)

Samples were selected close to the Rubtsovskaya embankment in Moscow weekly in the daytime in the course of two months. The analysis method consisted in introducing a prepared sensitive element into a cell containing water to be analyzed that had previously been diluted (pH 6.8) and in performing spectrophotometric indication of the analytical signal as stated in the text above. The results obtained are presented as a histogram (Fig. 4).

Analyzing the data of Fig. 4, we see that an abnormally high content of calcium was registered in the Yauza River water in the middle of March. It is obviously connected with snow and ice thawing, as well as with the period of active snow melting. The mean level of Ca^{2+} content during the spring period does not exceed 400 mg/l.

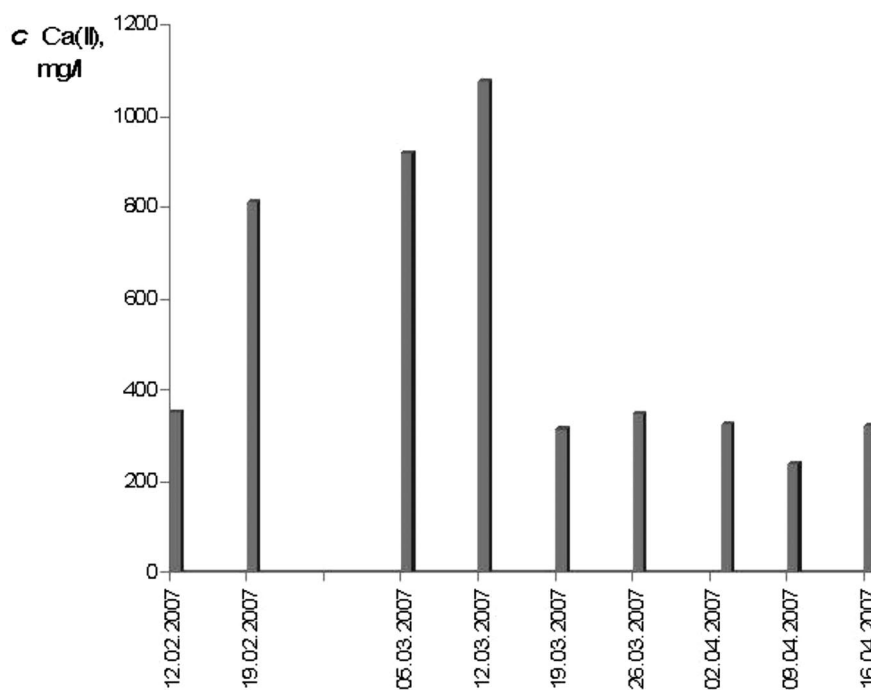


Fig. 4 Monitoring of Ca^{2+} content in the Yauza River water (Moscow, Russian Federation); $n = 10$; $P = 0.95$.

CONCLUSIONS

A method of synthesis of sensitive chemical-analytical elements (simplest devices) of a new type has been worked out, optimal conditions for calcium ion determination have been set, and data concerning its content in the Yauza River water (the Rubtsovskaya embankment) in the period of snow thawing have been obtained. The newly worked-out method permits us to quickly quantitatively (in the case of spectrophotometric detection) or semiquantitatively (in the case of visual indication) determine the content of calcium ions in water of any type.

Among the advantages of the method, we may consider simplicity and expressibility of determination and the possibility to preserve the colored matrix for a long time for further spectrophotometric indication in the laboratory. We may recommend that this test method should be used to check the content of calcium in water both in situ and in stationary laboratories that deal with ecological analysis.

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