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CALS-system of Ecological Monitoring of Road Anti-icing Materials on the Major Environmental Components

Andrey Glushko[a], Arkadiy Bessarabov[b], Georgiy Priorov[a,*]

[a]National Research Center "Kurchatov Institute" – IREA, st. Bogorodskii val 3, 107076 Moscow, Russian Federation
[b]R&D Centre "Fine Chemicals", Krasnobogatyrskaya st. 42, 107564 Moscow, Russian Federation
priorov@irea.org.ru

Two automated systems have been developed for the ecological monitoring of road anti-icing materials: a computer-aided quality management system for anti-icing materials, in which the environmental indicators have a big section; system of ecological monitoring of the influence of anti-icing materials on the most important components of the environment (snow cover, water objects and groundwater, soil cover, green plantations, atmospheric air). The systems are developed on the basis of information CALS-technologies.

1. Introduction

Anti-icing materials provide safety on the highways of the country. Given the geographical vastness of Russian Federation, its highways play a most important strategic role. Binding together territories by means of mass transfer of cargo and passenger transportation, and providing access to various recourses, highway infrastructure decisively facilitates the development of constituent territories of the Russian Federation. Highway transportation exceeds many fold (Figure 1) all other transportation systems as airborne, water-borne, and railroad, in terms of their key indicators as freightage, passenger carriage, length of communication lines, etc. (Glushko et al., 2015).

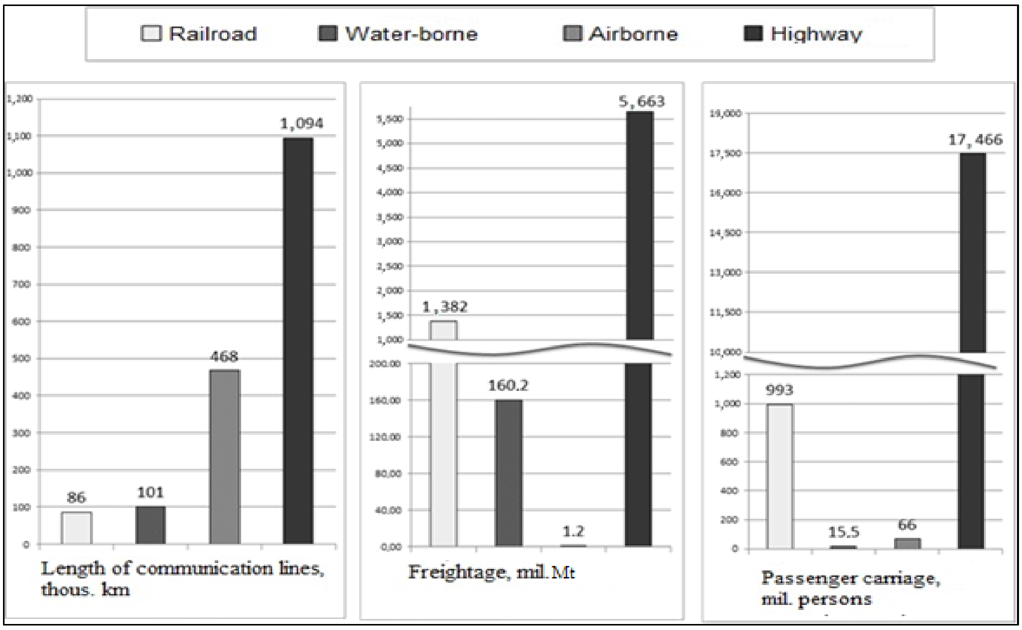

Figure 1: Comparative characteristics of Russian Federation transport systems

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However, today's quality index of Russia's road infrastructure is relatively small compared to other countries. With the increase in the quality index of highways, the indicator of their efficiency also increases. The index is derived from opinion polls among companies' executives and experts based on a scale from 1 to 7, where 1 is the lowest score (roads are very bad) and 7 is the highest score referring to a ramified and effective system of roads according to international standards. The quality of the road infrastructure of the Russian Federation currently has a low expert rating - 2.3 points (136 places) (Glushko et al., 2015). Alternatively, quality of roads can be measured using EUROSTAT's or World Bank's quantitative data: length of the road network (including length of local, long-distance and interstate roads), types of road pavements and the amount of asphalt- covered roads, and road density (ratio of the length of the country's total road network to the country's land area). The road-maintenance key objective is to increase the wheel-road adhesion factor in autumn and winter periods and, at the same time, preserve the quality of the bituminous concrete surface. With this aim in mind, chemical research institutions created anti-icing materials (AIM) that are used by highway services.
Every year in the world, huge amounts of AIM are used on roads and the possible environmental consequences from the use of reagents are actively discussed in the literature every year (e.g. Glushko et al., 2015). With increasing safety on the roads (with the help of AIM), negative environmental consequences are obtained. Despite certain disadvantages of AIM, there are no other alternative ways to combat with winter slipperiness. The issue of environmental safety of the currently used AIM is very relevant and there is a need for a detailed and systematic approach in assessing the potential impact of reagents on human and natural objects (Xing, 2017), as well as establishing the risks and limitations associated with the handling of these products. To solve these problems, the development of computer systems for environmental monitoring of the AIM and the influence of AIM on environmental objects is being carried out.

2. Computer management of the quality of environmental indicators of the AIM

The system of environmental monitoring of the AIM (Figure 2) was developed on the basis of the CALS-standard (Continuous Acquisition and Life-cycle Support) ISO-10303 STEP in the software package PSS Lite (Bessarabov et al., 2016). The PSS Lite configuration has a two-tier client-server architecture. The server is the "Local database server" module, which is included in the distribution package of the PSS client module. Any computer on which a PSS client is installed can act as a Lite database server.

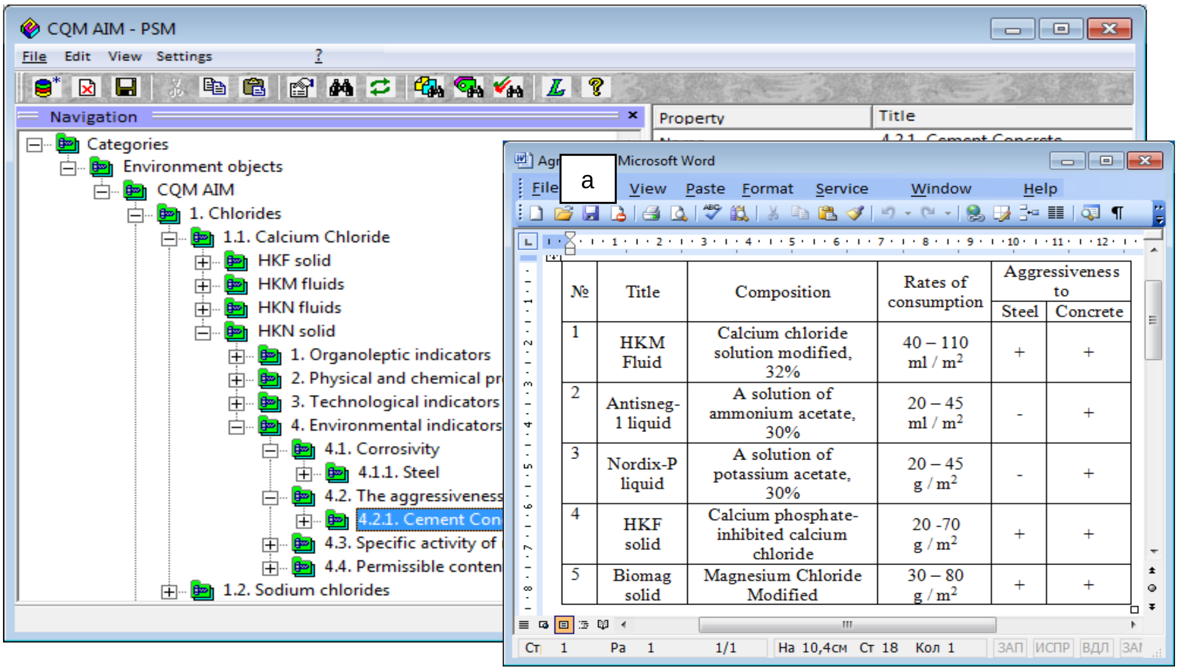

Figure 2: CALS-project of the CQM-system of AIM (a: AIM - chlorides - HKN solid - environmental indicators)

Based on the CALS conception of CALS, the computer-aided quality management system (CQM-system) of the AIM was developed (Figure 2). The CQM system of AIM shows the main quality indicators. They are grouped into four subcategories: organoleptic (appearance, color, odor), physicochemical (mass fraction of soluble salts, grain composition, crystallization start-up temperature, humidity, mass fraction water-insoluble substances, hydrogen index, density, dynamic viscosity), technological (melting capacity, hygroscopicity, caking) and environmental. Further the environmental indicators are described in more detail.

Environmental indicators include: corrosion activity on the metal, the index of aggressive impact on cement concrete, the specific effective activity of natural radionuclides and the permissible content of chemicals that are not related to the active substance of AIM. For each indicator in the CQM system, the corresponding laboratory equipment.

One of the most important factors is their aggressive effect on steel. Tests for corrosion activity are carried out gravimetrically on metal plates made of steel. For the measure of aggressive impact of AIM on metal, the rate of mass loss per unit area of the sample is accepted for a certain period of time. Gravimetric method also determines the aggressive impact on cement concrete.

The specific effective activity of natural radionuclides is an important indicator of the quality of anti-icing materials. The determination is carried out by radiometric method using the RKG-AT-1320A radiometer. The method is based on the measurement of radiation emitted by radioactive elements.

The last environmental indicator is the admixtures of substances that are not related to the active chemical composition of the AIM. This indicator includes the following components: water-soluble form of fluorine, gross content of zinc, lead, nickel, copper, mercury, molybdenum, cobalt, cadmium, chromium, selenium, arsenic. To determine these substances in the CQM system, two analytical methods are presented with the corresponding instruments: atomic emission spectroscopy and inductively coupled plasma mass spectroscopy.

3. The structure of the system of environmental monitoring of the AIM's impact

Based on the CALS conception, a computer-aided quality management system (CQM-system) was developed to assess the environmental impact of AIM on the environment (Priorov, 2017). Various environmental objects were selected as a top-level category (Figure 2): snow cover and water objects (category No. 1); soil cover (No. 2); green plantations (No. 3) and atmospheric air (No. 4).

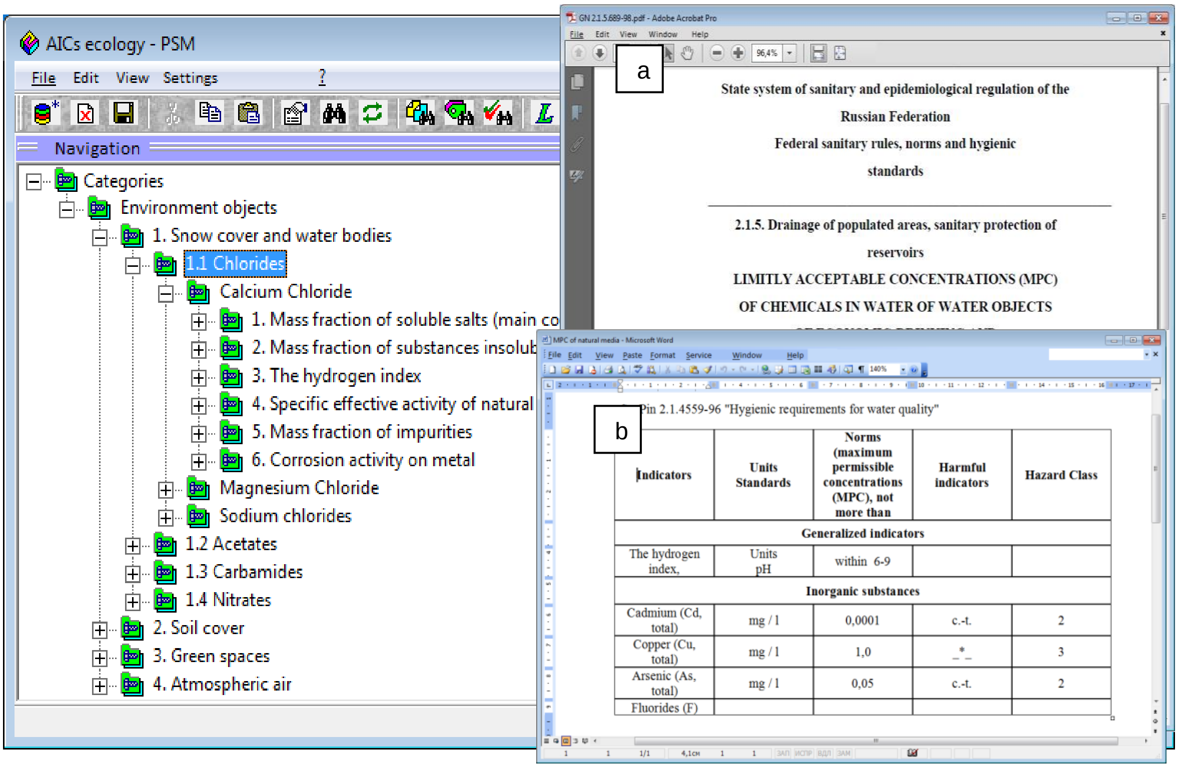

Figure 3: CALS-project "Environmental Impact of AIM". Snow, water bodies - Chlorides (a - hygienic standards 2.1.5.689-98, b - table of maximum permissible concentrations for water)

At the 2nd level of the developed system, the main groups of chemical AIMs are considered: chlorides, acetates, carbamides and nitrates (Achkeeva et al., 2014). The figure shows the element of the CALS project for subcategory No. 1.1. "Chlorides". In the considered sub-category of the 2nd level, three subcategories of the 3rd level are distinguished, which are the names of chemical substances - the main components of the AIM: calcium, magnesium and sodium chlorides. For each connection, 6 quality indicators characterizing the degree of exposure to the selected environmental object (Figure 3) are recorded in the system: the mass fraction of soluble salts (subcategory No. 1), the mass fraction of water insoluble substances (No. 2), the hydrogen index (No. 3), specific effective activity of natural radionuclides (No. 4), mass fraction of impurities (No. 5) and corrosion activity on metal (No. 6). For each indicator, the system records all the information necessary for the researcher on the method of determination used by the instrument and the type of output documentation. Determination of the mass fraction of soluble salts (subcategory No. 1) is carried out by the titrimetric method, for which several names of the digital burettes of various brands used for this purpose are given in the system (BRAND Titrette, BT-50 Stuart Scientific, etc.). As an example (Figure 3) the element of the CALS-project for the subcategory "Chlorides" is presented. It is shown that the main source of chlorides is sewage water, since the bulk of snow containing AIM components is utilized in them. Modern cleaning system does not allow to purify water from chloride ions. All incoming chlorides with AIM after water treatment from other pollutants fall into the rivers of Moscow. The mass fraction of substances insoluble in water (subcategory No. 2) is determined gravimetrically. The sample of AIM is filtered through an impure "blue tape" filter (previously dried in a drying cabinet at a temperature of 60 - 70 ^{0}C to constant weight). The filter cake is washed with hot water until a negative reaction to the chloride ion occurs, and then the precipitate filter is heat treated in a drying cabinet. In the CQM system, there are several options for drying cabinets of various manufacturing companies Ulab (China), Umega (Lithuania), Ekros (Russian Federation). This is convenient when choosing a drying device with different dimensions, maximum temperature and drying mode. In the CQM system, the determination of the hydrogen index (subcategory No. 3) corresponds to a potentiometric method (the device is a pH meter). The method is based on potentiometric measurement of the potential difference between a glass electrode and a reference electrode immersed in an aqueous solution of AIM. Determination of the specific effective activity of natural radionuclides (subcategory No. 4) is carried out by radiometry. The method is based on the measurement of radiation emitted by radioactive elements. The CALS-projects include data on various pH-meters and radiometers of domestic and foreign production.

4. Analytical monitoring of impurity components of chemical AIM

Analytical monitoring associated with the determination and entry into the CQM system of impurity components of chemical AIM is very important. For this purpose, three subcategories of the fourth level, united by the method for determining the impurities in question, are identified in the subcategory No. 5 "Mass fraction of impurities" (Figure 4).

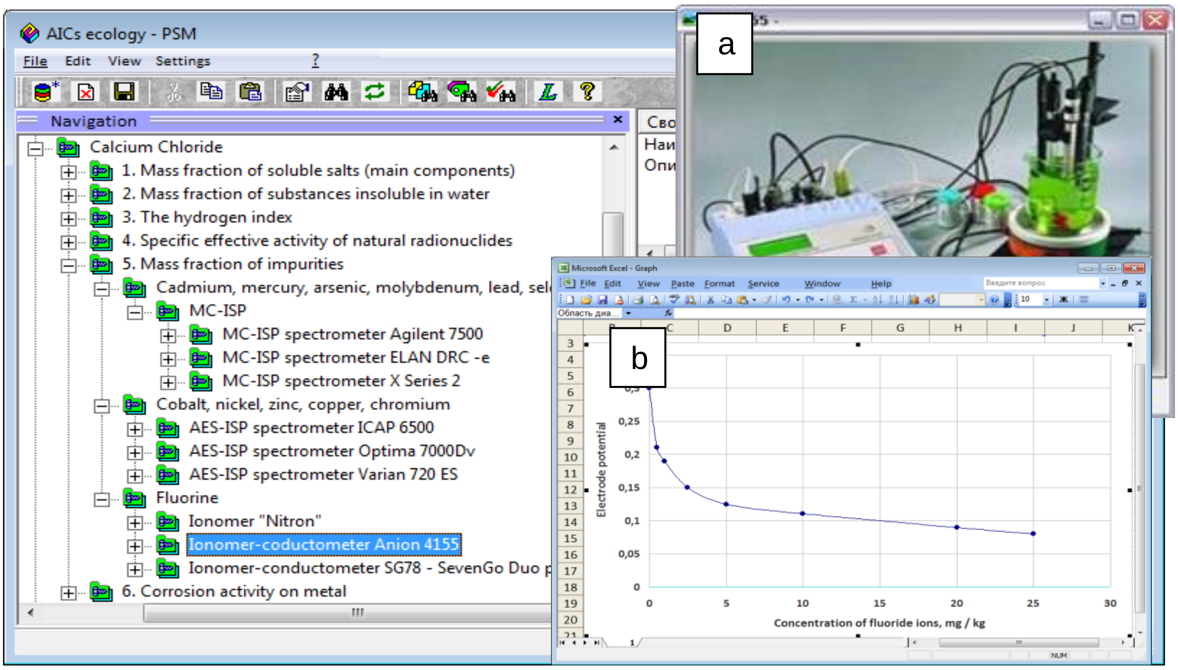

Figure 4: CALS-project "Environmental Impact of AIM". Calcium chloride - Impurity of fluorine (a - ionomer-conductometer Anion 4155, b - graph of the electrode potential)

The producers of anti-icing materials have sufficiently limited amount of the possibilities to effect on the content of these impurities. The quality of the reagent is mainly determined by the quality of the raw materials used. Various kinds of spectral analysis can be used to analyze impurities in the AIM, allowing simultaneous multiple element determinations. The most important of these are: atomic-emission spectrometry with inductively coupled plasma (AES-ISP) and inductively coupled plasma mass spectrometry (MC-ISP) method. For a complex solution of problems of qualitative analysis of AIM samples, it is expedient to use both methods, which makes it possible not only to monitor the correctness of the results obtained for individual elements by comparing them, but also to choose the optimal scheme for analysis.
Impurities Cd, Hg, Mo, As, Pb and Se are determined by mass spectrometry with inductively coupled plasma (the method is based on the use of a flare configuration for the ionization of inductive plasma elements, a quadrupole mass spectrometer is used to detect the ions of the elements being determined); Co, Ni, Cu, Cr, and Zn impurities by the method of atomic-emission spectrometry (the method is based on the use of a flame configuration as a source of excitation of spectra of the induction plasma, multichannel photoelectric systems are used to record the spectrum), and the fluorine impurity is used by potentiometry. As in the previously discussed subcategories, for each method in the system, several instruments of different development companies and types of output documentation are presented (Figure 4a).

5. Development of environmental AIM on the basis of sodium formate

The developed CQM systems "AIM" and "Environmental impact of AIM" are interrelated and complementary. This is well confirmed by the work on sodium formate - one of the perspective AIMs used in Moscow (Figure 5). One of the main reasons for using sodium formate is its positive environmental impact (Frolova et al., 2013).

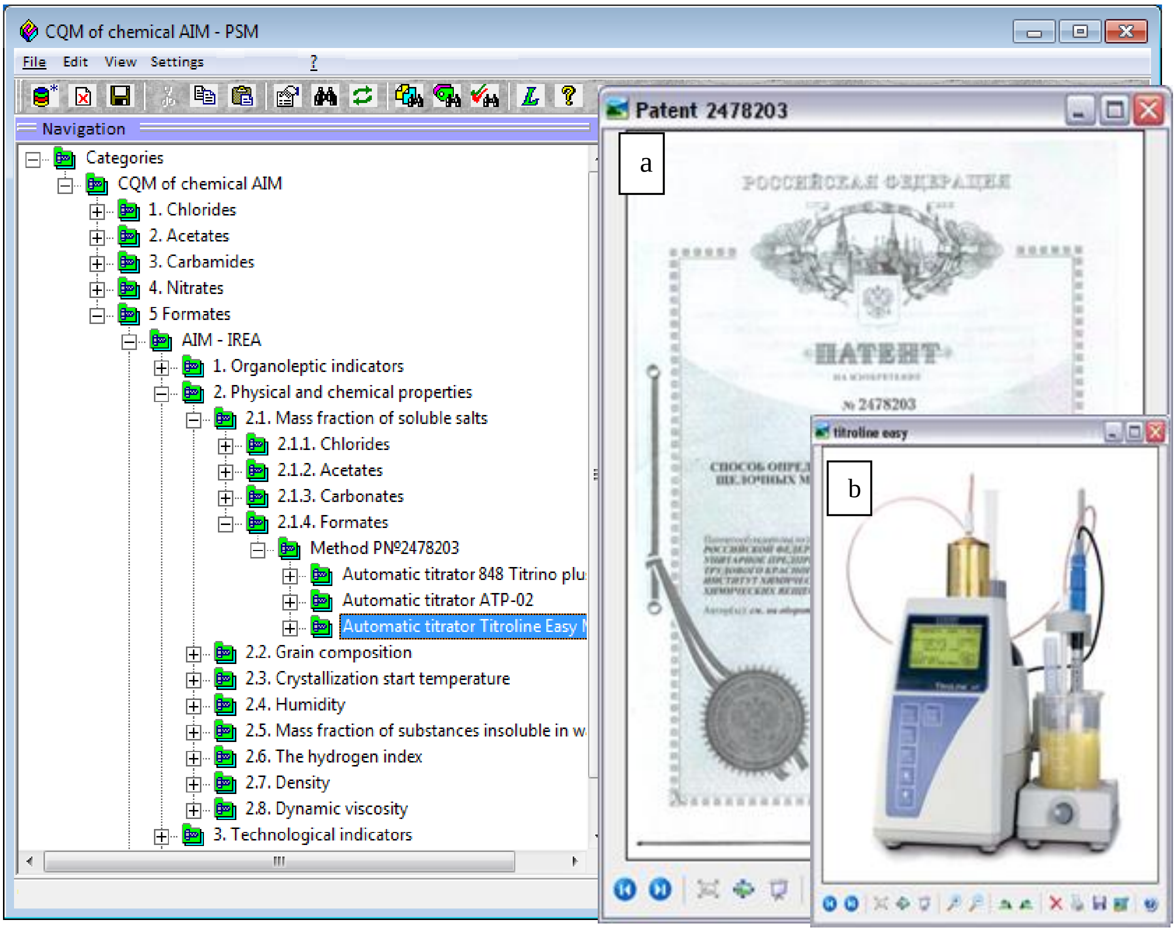

Figure 5: CQM-system for AIM. Physico-chemical indicators - determination of formates (a - patent on the method for determination of formates, b - titrator TitriniLine)

Sodium formate is a new active material used in the AIM formula. It has a number of advantages as compared with calcium chloride and sodium chloride, namely: much lower corrosion rate; chemical stability; resistance to aging at low temperatures of up to -20^0C. Its environmental impact is minimal, because when dissolved in water it undergoes complete biological degradation without causing any oxygen deficit in water environment.
For the quantitative determination of alkali metal formates in AIM, a new titrimetric method (Figure 5b) for the determination of alkali metal formates in anti-icing materials containing 1.0 to 50.0 % alkali metal formates and additionally containing calcium chlorides and alkali metal chlorides is introduced into the CQM system, which involves the treatment of an aqueous solution of the analyzed sample with an alkaline bromine solution having a bromine concentration of 0.1 mol/L, with the addition of glacial acetic acid to a pH of less than 1, maintaining the analyzed sample room temperature, followed by adding thereto hydrochloric acid solution of potassium iodide and titration with sodium thiosulfate pentahydrate at a concentration of 0.1 mol/l to light - yellow coloration, followed by addition of 0.5 % aqueous starch solution and titrating until complete discoloration. The practical significance of the studies is confirmed by the patent No. 2478203 of 27.03.2013. "The method for determining the content of alkali metal formate in anti-icing materials" (Figure 5-a).

6. Conclusions

On the basis of information CALS-technologies, computer-aided quality management systems for AIM have been developed in which environmental indicators have a big section. A CQM system for a new environmentally friendly formate AIM was developed. A new analytical method for the analysis of formates is implemented in the CQM system (protected by a patent). A system of environmental monitoring of the influence of anti-icing materials on the basic components of the environment was developed. For all quality indicators, the relevant analytical methods and analytical equipment have been introduced into the system.
The use of CQM systems allows the following: to improve analytical control in environmental monitoring; to guarantee the prompt provision of correct laboratory information; to increase the efficiency of using the resources of the analytical laboratory by 20 – 30 % (staff, instruments, reagents); to reduce the time for performing analytical studies (by automating the calculation of measurement results, generate reports and drawing up output documents on quality). The use of CALS-technologies allows using a complex of unified information models, standardization of ways of access to information and its correct interpretation based on the international CALS-standard ISO 10303 STEP.

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