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PASSIVE FILLERS FOR WATER ACTIVITY MEASUREMENT

The paper is dedicated to passive fillers, which are the necessary substances for a method of water activity determination in liquid samples by mirror dew-point temperature measurement. A number of such fillers for water activity analyzer Roremeter RM-10 are tested. The comparative analyses of their features and standard cellit-powder's characteristics is provided. The following fillers are recommended as the most effective replacers of cellit: carefully dried absorbent carbon, cleaved lignin, kaolin, silica-gel, pounded red and fire brick, and ceramic plate pieces.

Introduction. Currently, a number of instruments for water activity measurement in any products and materials are produced in different countries. Being compared with the classical method they are distinguished by high performance, ease of using, acceptable accuracy for practical applications. Most of them can't work directly with the liquid samples and require putting samples in a passive matrix of substance with developed surface. Most often, manufacturers use specially prepared costly matters [1, 2].

In this regard, this paper aims at solving the task of replacing imported passive filler for more accessible and cheap materials.

Main part. Control of parameter "water activity" (A_w) as an indicator of quality of water contenting food is carried out by measuring the dew point, the value of which is related to the magnitude of A_w [3]. The method of chilled mirror is used in the most effective means of measuring the thermodynamic characteristics. At this moment the sample is in equilibrium with the air environment of the measuring chamber. In the chamber there is a mirror, which is supplied with a Peltier cooler, and the optical device for detecting condensation that contains a light source, beam of which illuminates the mirror. A photocell detects the reflection and generates an informational signal when reflection falls due to condensation starting. In equilibrium, the relative humidity in the chamber has the same meaning as the water activity of the sample. In fact, to accelerate the process artificial ventilation is used in such devices that results in dynamic change of temperature. So, the equilibrium state is not reached, and the error relatively to the precision thermodynamic case appears. The error could be made insufficient by calibrating the instrument with standard samples.

The measurement accuracy provided by such devices at a temperature of the dew point above 0°C runs up to ±0.5°C. At lower temperatures, water or ice film is formed with delay and error can increases to several degrees. The protection against dust and other sediments of humidified mirror during the measurement presents some difficulties in dealing with such devices [1]. Impurity of the mirror provokes early condensation and leads to inflated measured values of the thermodynamic parameters of the sample.

Roremeter RM-10 (NAGY Messsysteme GmbH, Germany) is among the most common in Europe analyzers of water activity, and we used it in our experiments. It ensures high enough level of measurement results stability.

The purified powder cellite (alloy of cobalt, chromium, nickel and molybdenum oxides) is recommended as standard passive filler [4]. Production of this alloy is energy-intensive process that, along with the requirement to ensure its purity, stipulates its high cost. Therefore, the aim of our research was to study the possibility of using other porous chemically passive fillers.

We have analyzed different types of fillers: medical sorbents, clay minerals, ceramic products, dietary fiber and inert inorganic substances. Previously [1, 2], we have already tested various fabrics, which had good metrological characteristics, but insufficient absorption capacity, which often led to the formation of droplets or filtrate in the cell. In this regard, this paper deals with fine substances with very high developed surface. Among them, the following substances were investigated.

Activated carbon contains a large number of pores, and therefore has a very large surface squire per unit of mass, and consequently it demonstrates high water adsorption.

Powdered silica sand, grade B according to State Standard 9077 is marchalite used as a filler of suspensions for making molds in investment casting, as well as a component for electrode coatings.

Microcrystalline cellulose is fiber, derived from vegetable cellulose. According to its properties it is close to the natural pulp, which is in the form of a natural component in foodstuffs.

Hydrolytic lignin is obtained by deep processing of coniferous woods; it is medical enterosorbent.

Alumina is an inorganic adsorbent widely used in the technique for drying of different media and for other purposes. Alumina structure depends on the type of the original hydroxide, residual water content, the presence of oxides of alkali and alkaline earth metals as well as heat treatment conditions [5, 6].

In the literature, the term “clay minerals” often implies not only fine phyllosilicates, but also a number of other fine minerals, not always related to a subclass of layered silicates. Their classification is based on the following parameters taking into account: the ratio of tetrahedral and octahedral nets in structural package, fill pattern of octahedra in the octahedral layer, the size and position of the charge in the crystal lattice. We have analyzed the minerals of the kaolinite group (two-layer package dioctahedral fill pattern) and montmorillonite (three-layer package, dioctahedral fill pattern). Kaolin is a white clay, consisting of the mineral kaolinite $Al_4(OH)_8[Si_4O_{10}]$, whose basic properties are high fire resistance, low plasticity and binding capacity. In kaolinite hydrogen bonds between the hydroxyl groups of the octahedral network of one packet and oxygen of tetrahedral mesh in the next package provide for so strong interaction that the occurrence of water molecules, cations, or any other components into the inter-packet space becomes impossible. Therefore, kaolinite is not capable of inter-packet sorption of a substance.

To denote all minerals of montmorillonite the term “smectites” is used as a synonym in the world literature. It is derived from the Greek word "smektos", which means "soap" as aqueous suspensions of montmorillonite are soapy by touch. Generalized crystal-chemical formula of dioctahedral montmorillonite formula is presented as follows:

$$(Ca, Mg, ...)(Al,Fe^{3+}, Mg)_2(OH)_2[(Si, Al)_4O_{10}] \cdot nH_2O.$$

Due to low ion charge and weak electrostatic interactions between the three ply packet and inter-packet cations the minerals given are capable of inter-packet sorption of various substances such as cations, water molecules and many organic compounds [7].

Silica-gel is the dried gel formed from supersaturated solutions of silicic acid ($nSiO_2 \cdot mH_2O$) under $pH > 5–6$.

The conventional classification of ceramic materials and products is based on the pore structure. According to this classification the samples are divided into two main groups:

1) porous, with earthy fracture and leaking water;

2) sintered, giving lustrous conchoidal fracture and holding the water.

In addition, the products are classified by other features. According to the purpose in individual elements of buildings and structures, we used the wall products (bricks) and glazed tiles as the product for the inside lining the walls. Ceramic tile or glazed tile is usually rectangular plates of baked ceramics [8].

Crystal is lead silicate glass containing 13-30% or even more of lead oxide, and up to 17% of potassium oxides.

Sample preparation is usually limited only by grinding to a powder. However, hygroscopic substances require preliminary dehydration. In particular, the silica was calcined at 300°C for three hours. Dioctahedral smectite was washed of medicament followed by drying at 105°C for one hour. Aluminum oxide was calcined at 1200°C. Hydrolysis lignin was dried at 105°C for one hour.

Measurements were carried out at ambient temperature (25 ± 1)°C, where incubated samples were sustained at least one hour.

As a control, the activity value was taken for saturated solution NaCl with powder of cellite. All the data were compared with the tabulated value of the water activity of a saturated solution of NaCl, which is 0.7529 at 25°C. Instrumental error was not over 2%.

The results of the studies are presented in the table.

Average value of water activity of a saturated solution of NaCl for various passive fillers

Type of excipient	A_w
1. Cellite powder	0.763
2. Activated carbon	0.762
3. Marshalit	0.776
4. Microcrystalline cellulose	0.790
5. Hydrolytic lignin	0.949
6. .Hydrolytic dried lignin	0.764
7. Uncalcined aluminum oxide	0.824
8. Calcined aluminum oxide	0.798
9. Dioctahedral smectite	0.720
10. Kaolin	0.765
11. Silica gel	0.767
12. Technical Ceramics	0.774
13. Red brick	0.765
14. Firebrick	0.766
15. Tile	0.764
16. Crystal	0.756

The data in the Table show that with activated carbon, kaolin, silica, crystal, bricks and tiles as the filler, one can achieve the closest values of water activity of the control sample.

The lowest value of water activity is achieved with application of dioctahedral smectite. It has been shown quite a high value of water activity in the application of hydrolytic lignin, which indicates the high moisture of the original material.

The obtained results are partly affected by residual moisture in the samples. Thus, when drying of lignin, the water activity value originally contained in it, has decreased from 1.000 to 0.015. The calcination had less significant effect on aluminum oxide: the activity of the influent water decreased from 0.460 to only 0.433.

Conclusion. The work reveals that instead of celite powder one can use not only textile materials but other low-cost materials giving comparable with celite powder results. The most suitable alternate materials among investigated ones are activated carbon, lignin hydrolytic, kaolin, silica-gel, grated red and firebrick, fragments of ceramic tiles. To obtain the most accurate results, samples must be previously dried to remove residual moisture.

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