

# On the possibility of long-term storage of standard solutions

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## ABSTRACT

The possibility of long-term storage of standard solutions which do not react chemically with air and with the vessel walls was studied for 3 types of the vessels. In this case, a change in concentration can occur only due to the water evaporation. The amount of evaporated water and thus the concentration change was determined over time on a balance by the decrease of the vessel mass. It was established that, if some precautions were taken, standard solutions may be stored for a long time (many months) in glass volumetric flasks and in PE vessels without significant change of their concentration. Some aspects of the volumetric trilon titration of metals, its precision and accuracy of the standard solutions are discussed. It is shown that when analyzing metal salt hydrates, it is possible to find the water content with acceptable accuracy by determining only one component (metal). But this determination should be carried out with high precision ( $\pm 0.1$  rel. %). This also requires the preparation of standard metal solutions with the same accuracy. The most convenient method for that is to prepare their salts and salt hydrates with a high degree of stoichiometry. Examples of such salts are given. The method of controlled isothermal drying of the higher salt hydrates can be used to synthesize these salts. The main difference between such drying and conventional drying is the necessity to record the composition of the sample in the former method. Using the results obtained earlier for the processes of thermal decomposition of the lower  $\text{LaCl}_3$  hydrates, a clear thermodynamic

justification of the method of controlled isothermal drying is given. It was found that long-term storage of standard solutions in PET bottles is impossible due to the permeability of their walls to the water vapour. It is also impossible to store hygroscopic substances in such bottles.

**KEYWORDS:** standard solutions, chemical analysis, synthesis, derivatography, isothermal drying, solutions storage.

## ABBREVIATIONS

PET – polyethylene terephthalate  
PE – polyethylene  
Trilon – dihydrate ethylenediaminetetraacetic acid disodium salt,  $\text{EDTA-Na}_2$

## 1. INTRODUCTION

It is widely believed that long-term storage of standard solutions should not be allowed because when standing, they change their concentration [1]. We conducted our own research to determine the time of possible storage of such solutions without significant changes in their concentration. In doing so, we proceeded from the fact that all our solutions were chemically stable in air and could not interact with the material of the vessels. Therefore, a change in the concentration of solutions could occur only due to the evaporation of water. The answer to this question should obviously depend both on the required accuracy of the analysis and the standard solutions, and on the properties of the vessels in which such solutions are stored. In this connection the article discusses some issues related to the precision of

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analytical determinations by the volumetric method and the accuracy of chemical standards, as well as the possibility of standard substance synthesis in a chemical laboratory. As for the vessels, 3 types are considered for storing standard solutions - in glass volumetric flasks (for small volumes of these solutions) and in two types of plastic vessels. The results obtained are sometimes rather surprising and contradict some of the ideas prevailing in science and in everyday life.

## 2. MATERIALS AND METHODS

### 2.1. Vessels and solution storage conditions

For the preparation and storage of standard solutions, glass volumetric flasks (0.25–1 L), PET bottles (0.5–2 L), and PE bottles (2–3 L) were used. The glass stoppers were carefully ground to the volumetric flasks and good results were obtained with PE stoppers. Vessels with the solutions were stored in a not tightly closed laboratory bench at the air temperature of 18–25 °C and at the relative humidity of 50–60 %. They were periodically weighed on two types of electronic balances: with a maximum load of 6 kg ( $\pm 0.1$  g) or 400 g ( $\pm 0.01$  g). When taking samples and moving the vessels, it was necessary to ensure that the solution did not get on the thread or the section of the plug. If this happened, then the rate of the mass decrease of the vessel during its storage increased sharply due to the capillary rise of the entrained solution to the surface of the plug. Therefore, in this case, the plug and the neck of the vessel were thoroughly wiped dry.

### 2.2. Precision and accuracy of analysis

When studying the physicochemical properties of chemical compounds, it is very important to have a reliable information about their stoichiometric composition. Even relatively small deviations from stoichiometry can, as is known, very significantly affect some properties of a substance, such as electrical conductivity, its magnetic, optical, catalytic and other properties. The lack of reliable data on the chemical composition of the studied substance can devalue the results of the most accurate measurements of its physical and chemical properties.

Our research has shown that for the preparation of standard solutions, we cannot use the modern standard titers produced in Russia, because they have an

accuracy of  $\pm 1$  rel. % [2, 3]. This is quite consistent with the requirements of process control in the industry, but does not meet our needs.

In our studies of the formation processes, thermal stability and thermodynamic properties of the metal salt hydrates [4-9], it was necessary to determine the hydration water content as accurately as possible. There are many methods for determining the water content in various materials [10], all of them are very laborious and do not always provide the required accuracy of the results as applied to the solid hydrates of metal salts.

We have previously shown [11, 12] that a completely satisfactory accuracy of water analysis ( $\pm 1$  rel. %) can be obtained by determining only one component — metal. This is on par with the best direct methods for determining water. However, for that it is necessary to ensure a very high accuracy of the metal determination ( $\pm 0.1$  rel. %). Such a random error in titration with a standard trilon solution is quite achievable if you first work out the titration procedure on the standard solutions and take 5-7 aliquots each time. In this case, readings should be taken on a 25 mL burette with an accuracy of  $\pm 0.01$  mL. But the final result of the determination also includes a possible systematic error of the trilon standardization, which should also be at the level of  $\pm 0.1$  rel. %.

Hence it follows that it is necessary to prepare in the laboratory the primary standard solutions of the metal salts with such accuracy. This can be achieved, in particular, by the synthesis of some salts with a strictly stoichiometric composition. A derivatographic study of their higher hydrates was first carried out [5, 13] at a possibly low heating rate (0.7–4.5°/min for 0.2–0.5 g samples). Then the technique was worked out using the method of controlled isothermal drying of samples. In such a way, good results were obtained for the following salts: Ca (HCOO)<sub>2</sub>, Mn (HCOO)<sub>2</sub>, CuCl<sub>2</sub>·2H<sub>2</sub>O, LaCl<sub>3</sub>·3H<sub>2</sub>O, La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O, CuCl, KCl [14-18]. At the same time, for some salts recommended in [19], we failed to obtain results of acceptable accuracy.

The highest accuracy of titration results in 2 more circumstances, which we had to take into account in the analysis. First, the temperature must be taken into account; when it changes, the concentration of the solutions changes noticeably. For example,

calculations based on the data of [20] show that on going from the temperature of 10 °C to 30 °C, the concentration of a 0.1 mol/L solution decreases by a very significant amount of 0.4%. The temperature of all solutions in the laboratory was the same; it was necessary to measure it with an accuracy of  $\pm 0.5^\circ$ . It can be easily shown that it is sufficient to determine the temperature only once - when preparing the primary standard solution, which was used to standardize the trilon solution. We brought the concentration of this solution to the standard calibration temperature of the volumetric glassware of 20 °C. Then, regardless of the temperature in the laboratory, the results of all subsequent titrations also refer to the temperature of 20 °C.

Secondly, when titrating different primary standard solutions with trilon, different indicators were used - eriochrome black, murexide and xylenol orange. All three indicators give a fairly clear colour transition at the endpoint of the titration, and theoretically the titration results should not depend on the choice of indicator. However, in practice, we felt very small (0.2-0.3 %), but systematic differences in the concentration of trilon, established with different indicators. These differences are significant and have to be taken into account in the accurate titration - the concentration of the same standard trilon solution turns out to be slightly different when titrating with different indicators.

### 2.3. Preparation of standard solutions

All the reagents used in the work were "chemically pure" or "analytical grade". The metal samples (Zn, Cd, Al, Cu) used to prepare standard solutions had a purity of four to five 9s, while Zn and Cd were sublimed in a high vacuum, and copper was heated in a hydrogen atmosphere. To prepare the standard solutions, samples of metals and of metal salts synthesized in the laboratory were weighed on an analytical balance ( $\pm 0.1$  mg), if necessary in the closed wide glass weighing bottles.

When dissolving highly pure metals (Zn, Cd, Al) in dilute HCl, care had to be taken, because dissolution occurs very slowly, and when heated, loss of the substance can be observed due to its entrainment in the droplets of the formed fog. Good results were obtained by adding a piece of Pt strip to the metal being dissolved - dissolution is faster, but it can still take several days.

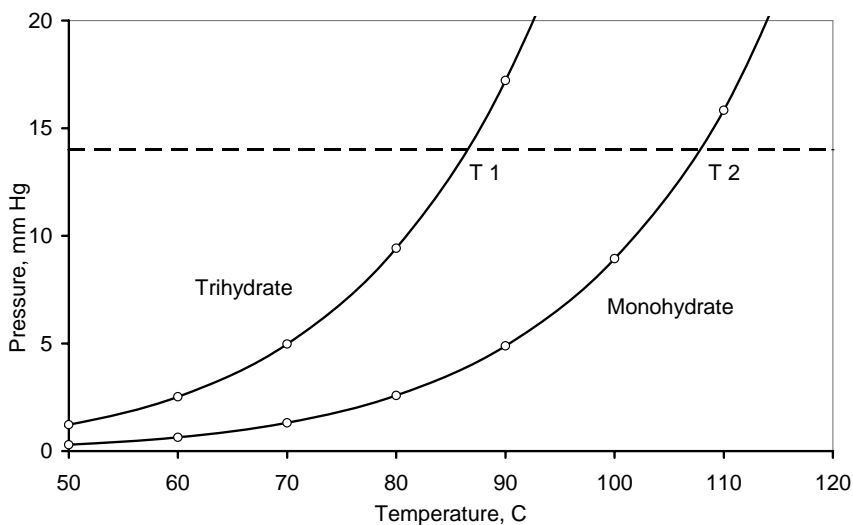
It turned out to be more convenient to prepare primary standard solutions from their highly water-soluble salts with a high degree of stoichiometry. For their synthesis, the method of controlled isothermal drying proved to be most useful (see below).

Volumetric flasks and pipettes were calibrated by the weight of water ( $\pm 0.01$  mL). Trilon was used as a titrant in determining the content of metals in the salts and their hydrates. The initial working solution of trilon with a nominal concentration of 0.025 mol/L was prepared in an amount of 5-10 L in PE canisters by dissolving a certain weighed portion of trilon in a calculated amount of heated distilled water. After allowing the solution to stand for several days, it was bottled for use and long-term storage.

### 2.4. Method of controlled isothermal sample drying

The method of controlled isothermal drying of hydrates was used in our work to obtain information on the stability of the lower hydrates, for their synthesis and study of thermal stability. Lower hydrates and anhydrous salts were obtained by the controlled isothermal drying of weighed portions of higher hydrates ( $4 - 10 \pm 0.0001$  g) in the wide glass weighing bottles in a drying oven. The drying temperature was measured and controlled with an accuracy of  $\pm 1^\circ$ . Each cycle of isothermal drying lasted 1-3 h, then drying was repeated many times (usually 10-20 times) at the same or at a different temperature. The composition of the obtained products was calculated from the loss of water mass and controlled by their chemical analysis for the metal content. Preliminary information on drying conditions was obtained as a result of a derivatographic study of the samples.

The results obtained to date for the lowest hydrates of lanthanum trichloride make it possible to consider the physicochemical foundations of this method and give its thermodynamic substantiation. In Fig. 1 two curves of the temperature dependence of the thermal decomposition pressure of the lowest hydrates of lanthanum chloride are presented. They are constructed according to the data given in [9]. The dotted line shows the approximate value of the water vapour pressure in the laboratory (it corresponds to a humidity of 60% at the temperature of 25 °C).



**Fig. 1.** Thermal decomposition pressure of  $\text{LaCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ .

From the theory of thermodynamic equilibrium it follows that at temperatures below T1 (approximately 87 °C), the trihydrate should not decompose, because it is thermodynamically stable. Naturally, the value of this temperature depends on the air humidity in the laboratory. Above this temperature, the trihydrate must decompose to the monohydrate, which in turn must also decompose to the anhydrous trichloride above T2 (approximately 108 °C). Thus, stoichiometrically pure  $\text{LaCl}_3 \cdot 3\text{H}_2\text{O}$  can be obtained by drying only at the temperatures below 87 °C. However, it should be borne in mind that the lower the temperature, the lower the rate of the dehydration process.

Monohydrate  $\text{LaCl}_3 \cdot \text{H}_2\text{O}$  can be obtained only in a relatively narrow temperature range of 87-108 °C. Consequently, to obtain a complete picture of the dehydration of the higher hydrate of lanthanum chloride  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ , its drying must be carried out at different temperatures. This is the meaning of the method of controlled isothermal drying - it is necessary to control both the drying temperature and the composition of the formed solid. In essence, this method is quite similar to the derivatographic method, but only the heating rate is very low, i.e. the results obtained should be much closer to the thermodynamic equilibrium. By changing the temperature during isothermal drying, one can significantly change the picture of the dehydration process and the composition of the formed hydrates. Moreover, the synthesis of some lower hydrates

can be carried out only in very narrow temperature ranges. It is clear that the derivatographic method, even at its lowest rates, can miss the plateau of formation of the monohydrate  $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ .

The above theoretical analysis of the data shown in Fig. 1 is fully supported by the available experimental data for the controlled isothermal drying of  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ . As an example, Fig. 2 shows the process of dehydration of the higher hydrate of lanthanum chloride at two temperatures: first at 80 °C and then at 100 °C. In this case, a clear plateau is obtained both for the trihydrate and for the monohydrate.

### 3. RESULTS AND DISCUSSION

#### 3.1. Storage of solutions in glass volumetric flasks

Table 1 shows the results of storage in 0.25 L glass volumetric flasks of two standard  $\text{La}^{+3}$  solutions with a volume of about 150 mL: sulfate (in flask 1 with a well-ground glass stopper) and chloride (in flask 2 with a tightly inserted PE stopper).

We see (line 4) that the concentration of the standard solution in flask 1, even after almost 9 months of storage, increased very insignificantly due to the evaporation of water – only by 0.13 rel. %. In conventional titration ( $\pm 1$  rel. %), such a change in concentration can be neglected altogether, and in accurate titrations, the corresponding correction can be easily obtained using the equation

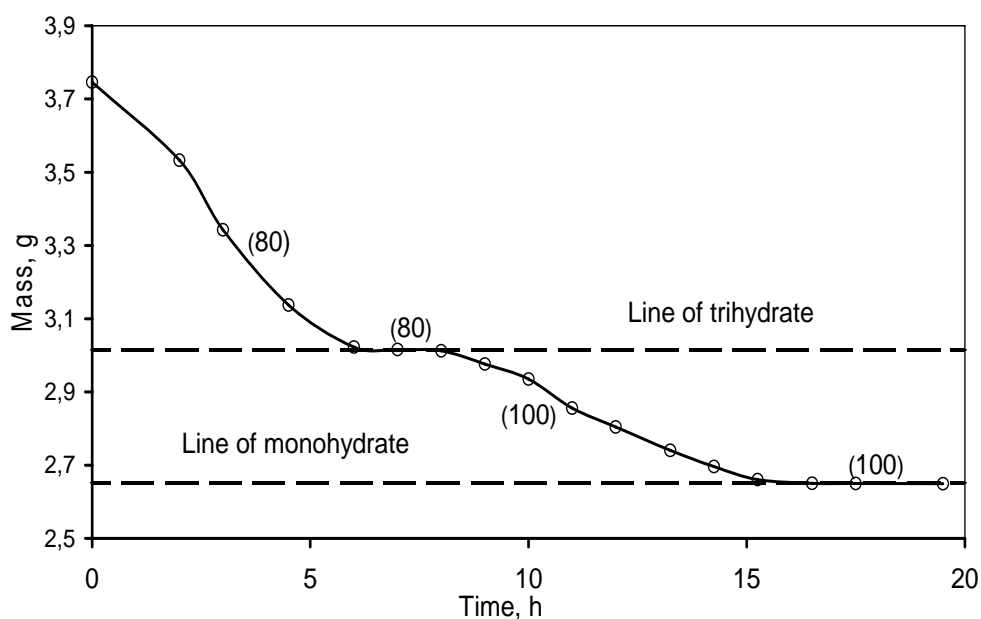


Fig. 2. Dehydration curve of the  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  sample (3.7461g).

Table 1. Storage results for two  $\text{La}^{+3}$  standard solutions in glass volumetric flasks.

N <sub>2</sub>	Total time (days)	0	41	150	174	238	265
1	Flask 1 mass	356.68	356.67	356.58	356.58	356.53	356.48
2	Total $\Delta V$ , mL	0	-0.01	-0.10	-0.10	-0.15	-0.20
3	C(mol/L)	0.025234	0.025236	0.025251	0.025251	0.025259	0.025268
4	Total $\Delta C$ , rel.%	0	0.007	0.07	0.07	0.10	0.13
5	Flask 2 mass	433.58	433.58	433.58	433.58	433.57	433.56
6	Total $\Delta V$ , mL	0	0	0	0	-0.01	-0.02
7	C(mol/L)	0.024153	0.024153	0.024153	0.024153	0.024155	0.024156
8	Total $\Delta C$ , rel.%	0	0	0	0	0.007	0.013

$$C_t = C_0 \cdot 150 / V_t, \quad (1)$$

where  $C_0$  is the initial concentration of the solution,

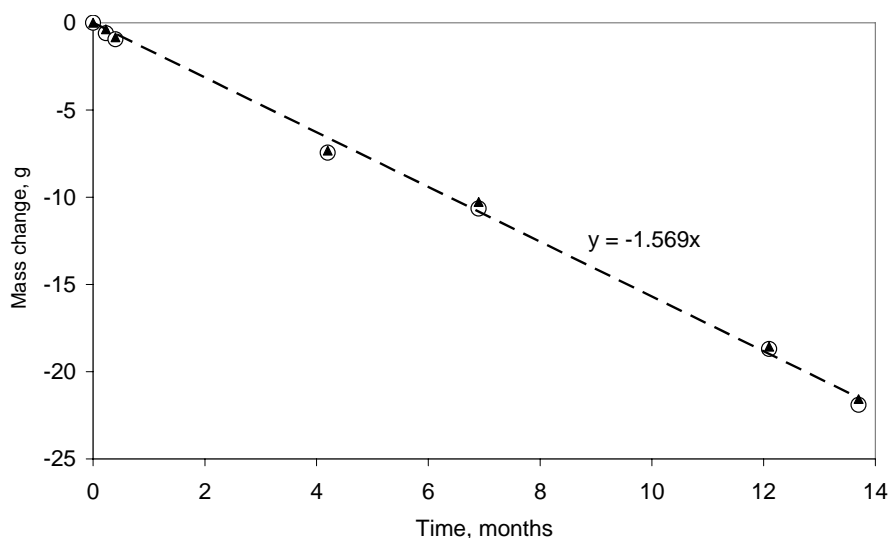
$C_t$  - concentration at a given time,

$V_t$  is the volume of the solution, decreased (in mL) by the value of  $\Delta V$  (line 2), numerically equal to the mass (in g) of the water evaporated by the given time.

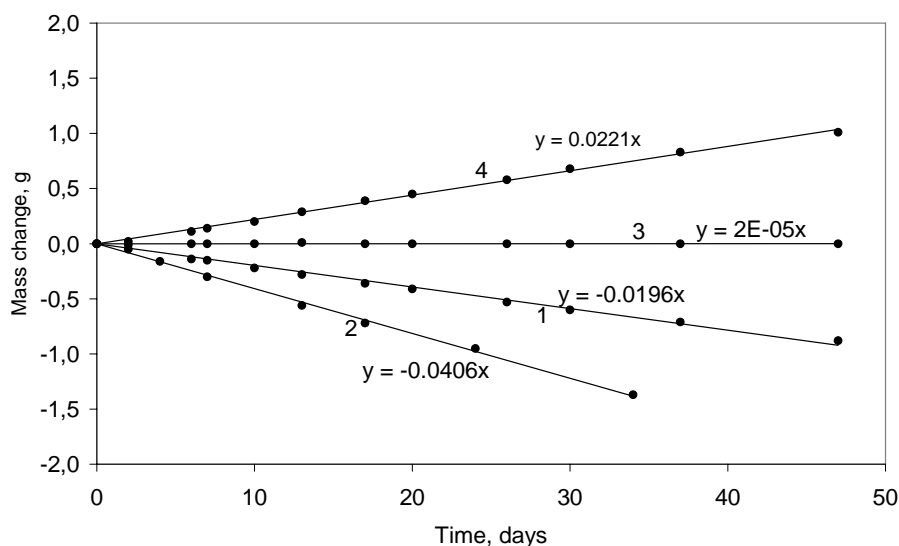
Even more surprising results were obtained for flask 2, tightly closed with a PE stopper. In this case, the flask turned out to be closed almost hermetically, and the evaporation of water through the ground joint was so insignificant that it could be neglected in the most accurate titrations.

### 3.2. Storage of solutions in PET bottles

Two series of experiments were carried out using PET bottles. In the first series, 5 identical 2-liter bottles were used: three of them each contained 1.3 liters of the standard trilon solution; in the other two - 1.9 liters of the standard solution of magnesium sulfate. These solutions were prepared from the standard titers and had a concentration of approximately 0.025 mol/L. The bottles were tightly closed with the standard screw caps. During the storage of these bottles, it was found that their weight noticeably decreased over time, and for all 5 bottles it was almost the same, with a small



**Fig. 3.** Mass change of standard solutions stored in PET bottles.



**Fig. 4.** Mass change of PET bottles during storage: 1 - 0.5 L with water, 2 - 1 L with water, 3 - 0.5 L empty (for control), 4 - 0.5 L with anhydrous  $\text{CaCl}_2$ .

scatter. The results obtained are shown in Fig. 3 - there are given the average values of the weight reduction of 3 bottles with trilon (black triangles) and 2 bottles with magnesium sulfate (open circles).

As can be seen from the equation shown in this figure, the decrease in the mass of the solutions at 1 month was 1.57 g, and by the end of the shelf life (13.7 months) - 21.5 g. This corresponds to an increase in the concentration of the trilon solution by 0.12

and 1.7 rel. %, and a larger volume of magnesium sulfate solution by 0.08 and 1.1 relative. %.

Even more illustrative results were obtained in the second series of experiments (Fig. 4). Here lines 1, 3 and 4 correspond to the 0.5 liter bottles with distilled water, empty and with anhydrous  $\text{CaCl}_2$ , respectively, and line 2 to 1 liter bottle with water.

We see that the rate of water loss increases with the volume of the bottle (the surface of the walls

**Table 2.** Storage results for the trilon standard solution in two PE bottles.

№	Total time (months)	0	2	15	19
1	Bottle 1 mass	3004.0	3003.6	3002.0	3001.9
2	Total $\Delta V$ , mL	0	-0.4	-2.0	-2.1
3	C(mol/L)	0.024905	0.0249083	0.024922	0.024922
4	Total $\Delta C$ , rel. %	0	0.013	0.07	0.07
5	Bottle 2 mass	1228.1	1227.6	1225.3	1224.7
6	Total $\Delta V$ , mL	0	-0.5	-2.8	-3.4
7	C(mol/L)	0.024905	0.0249175	0.024975	0.024990
8	Total $\Delta C$ , rel. %	0	0.05	0.28	0.34

increases). After 1 month, the water loss in the small bottle was 0.6 g, and in the large bottle - 1.2 g, i.e. the concentration of the solutions in these bottles could increase by 0.1 rel. % or more, depending on the volume of the stored solution.

The fourth bottle contained anhydrous  $\text{CaCl}_2$ , which is widely used as a desiccant. In this bottle, the air humidity was practically zero, and the process of diffusion of water vapour went in the opposite direction - from the outside air into the bottle. The diffusion rate in both directions was practically the same, as can be seen from the coefficients of the equations for lines 1 and 4. This experiment allows us to draw 2 interesting conclusions: first, it is impossible to store hygroscopic substances in PET bottles for a long time, because they can absorb moisture from the air. Secondly, the process of transferring water through the PET wall is vapor diffusion, not pervaporation, because for the fourth bottle the liquid phase of water was completely absent.

### 3.3. Storage of solutions in PE bottles

Table 2 shows the results of storage of two identical standard trilon solutions with different volumes (about 3 L – bottle 1 and about 1L – bottle 2) in identical PE bottles of 3 liters.

We see (line 4) that the concentration of the standard solution in vessel 1, even after 1.5 years of storage, increased due to the evaporation of water by a value less than 0.1 rel. %. In the second vessel, the loss of water was somewhat greater, and the volume of the stored solution was 3 times less, so the relative increase in concentration turned out to

be greater, about 0.3 rel. %. As with glass volumetric flasks, this small change in concentration can be neglected when titrating in industrial laboratories ( $\pm 1$  rel. %). For the accurate titrations, the corresponding correction can be easily obtained using the equation of the type (1).

### 4. CONCLUSION

Standard solutions can be stored in volumetric flasks for a very long time (many months), provided certain precautions are taken and their weight is constantly monitored on a balance ( $\pm 0.01$  g).

PET bottles are not suitable for long-term storage of standard solutions due to the permeability of the walls to water vapour. When hygroscopic substances are stored in such bottles, they can absorb moisture from the air.

Good results were obtained when the solutions were stored in tightly closed PE bottles. The storage time can reach many months and even years if a small correction is introduced for the increase of the solution concentration due to the evaporation of water.

Since the result of storage depends on many conditions, if it is necessary to store standard solutions for a long time, it is recommended to perform a set of studies in the laboratory similar to those given in this publication. In any case, it is necessary to control the mass of the vessels over time.

If it is necessary to synthesize metal salts with a high degree of stoichiometry for the preparation of primary standards of increased accuracy, we can recommend using the method of controlled

isothermal drying of their hydrates described in this article.

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### CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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