Determining of Age of artistic Paints by Measuring of H_2O Contents

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The method determining age of artistic paints is proposed. It is based on the use of closed Markov's graphs with three cells. The measurements of contents of water molecules in surrounding area can be done only for the space in which artistic paint is located. This means that method is nondestructive.

Keywords: *Humidity concentration, closed Markov's graph, age of artistic paint, distribution frequencies.*

1. INTRODUCTION

Determining of age of artistic paints is very important problem. This problem becomes very serious since the number of forgeries and forgers increases permanently. Control whether the paint is original or forgery is complicated by the fact that during analysis the paint should not be damaged.

It is the reason why we propose a method which is not destructive (in the sense of damaging of the artistic paint). The method consists in determining of humidity contents i.e. in measuring of ppm of molecules H_2O expressed in percents. This method is applicable in all cases, because the paint and its environment always contain some percent of molecules H_2O. The paint and environment exchange molecules of H_2O and therefore humidity percent changes in time.

We shall consider the case when the artistic paint remains in the same room. Since the room is not hermetically isolated of wider environment this fact must be taken into account from the moment of creation. It is obvious that the exchange of H_2O molecules between room and wider environment influences the humidity of the artistic paint.

The Marcov's graphs will be used [1] in calculations. The graphs will have three cells and will be closed. The cells correspond to the paint, to the room and to wider environment. The fact that the system is closed means that the sum of concentrations will be constant in time. The choice of closed system in the same time means that the effects of absorption of H_2O molecules by walls, furniture etc. are neglected, although they really exist.

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2. BASIC FORMULAS DETERMINING HUMIDITY

In the previous section it was said that the analysis will be based on closed Marcov's graphs with three cells. The mentioned graph is given on Fig. 1.

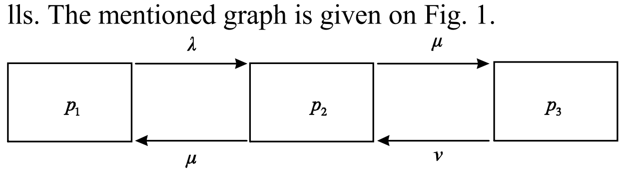

Figure 1 - The closed Marcov's graph with three cells

On this graph p_1 represents concentration of H_2O molecules in the artistic paint, p_2 is concentration of H_2O molecules in the room while p_3 is concentration H_2O molecules in wider environment.

Scheme on Fig. 1. represents graphical algorithm for forming the system of differential equations determining time dependence of concentrations p_1, p_2 and p_3. This system is as follows:

$$\dot{p}_1 = - \quad _1 + \quad _2$$

$$\dot{p}_2 = - 2 \quad _2 + \quad _1 + \quad _3 \qquad (2.1)$$

$$\dot{p}_3 = - \quad _3 + \quad _2$$

where *λ, μ, ν* are distribution frequencies. Summing these equations we obtain that

$$\dot{p}_1 + \dot{p}_2 + \dot{p}_3 = \frac{d}{dt}(p_1 + p_2 + p_3) = 0$$

wherefrom it follows that:

$$p_1(t) + p_2(t) + p_3(t) = const. \qquad (2.2)$$

The last formula is the proof that Marcov's graph is closed.

The system of differential equations (2.2) can be translated into system of linear algebraic equations by means of Laplace's transformation [2].

It means that all equations of the system (2.1) will be multiplied with $e^{-\omega t}dt$ and integrated with respect to t from zero to infinity. The described procedure gives the system of algebraic equations:

$$(\omega + \lambda)q_1(\omega) - \mu q_2(\omega) = p_1(0)$$
$$-\lambda q_1(\omega) + (\omega + 2\mu)q_2(\omega) + \nu q_3(\omega) = p_2(0)$$
$$-\mu q_2(\omega) + (\omega + \nu)q_3(\omega) = p_3(0) \qquad (2.3)$$

The notation used in (2.3) is:

$$q_s(\omega) = \int_0^\infty dt\, e^{-\omega t} p_s(t), \quad s = 1,2,3 \qquad (2.4)$$

The formula:

$$q_s(\omega) = \int_0^\infty dt e^{-\omega t} \dot{p}_s(t) = \omega q_s(\omega) - p_s(0), \quad s = 1,2,3 \qquad (2.5)$$

was used, too.

The solutations of the system (2.3) are given by:

$$q_1(\ ) = \frac{p_1(0)\ ^2 + [(2\ +\ )\ _1(0) +\ _2(0)]\ +}{\omega(\omega -\ _1\ \omega -\ _2}$$

$$q_2(\ ) = \frac{p_2(0)\ ^2 + [(\ +\ )\ _2(0) +\ _1(0) +\ _3(0)]\ +}{\omega(\omega -\ _1\ \omega -\ _2}$$

$$q_3(\ ) = \frac{p_3(0)\ ^2 + [(2\ +\ )\ _3(0) +\ _2(0)]\ +}{\omega(\omega -\ _1\ \omega -\ _2} \qquad (2.6)$$

where $H = p_1(0) + p_2(0) + p_3(0)$ and

$$\Omega_1 = -\frac{2\mu + \nu + \lambda}{2} + \frac{1}{2}\sqrt{4\mu^2 + \nu^2 + \lambda^2 - 2\nu\lambda} \qquad (2.7)$$

$$\Omega_2 = -\frac{2\mu + \nu + \lambda}{2} - \frac{1}{2}\sqrt{4\mu^2 + \nu^2 + \lambda^2 - 2\nu\lambda} \qquad (2.8)$$

Time dependance of concetrations $p_s(t)$; $s = 1,2,3$ can be found by application of inverse Laplace transformation [3]:

$$p_s(t) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} d\omega e^{\omega t} q_s(\omega), \quad s = 1,2,3 \qquad (2.9)$$

The contour in complex ω plane for calculation of Bromvich integral [5,6] is given on Fig.2

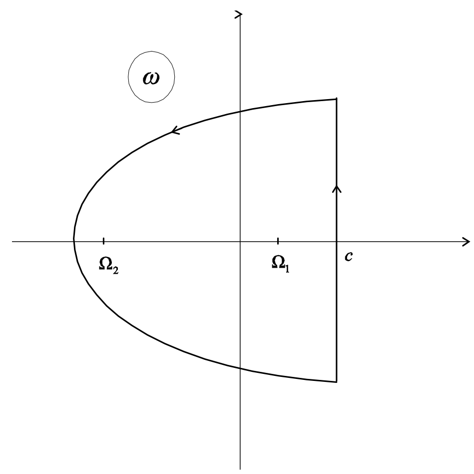

Figure 2 - Contour in complex plane for finding of inverse Laplace transformation

Since all functions $q_s(\ )$ have three simple poles $\omega = 0, \omega = W_1\ i\ \omega = W_2$, the integral (2.9) is sum of residues in poles $0, W_1$ and W_2. The formula for finding of residuum at simple pole is:

$$\operatorname*{Res}_{z \to z_0} f(z) = \lim_{z \to z_0}(z - z_0)f(z) \qquad (2.10)$$

Applying the formulas (2.9) and (2.10) to (2.6) we obtain the solutions of the system of diferential equations (2.1)

$$p_1(t) = \frac{\mu\nu H}{\Omega_1\Omega_2} + \frac{p_1(0)\ _1^2 +\ \ +\ _1\ +\ _2\ \ _1 +}{\Omega_1(\Omega_1 - \Omega_2)} e^{\Omega_1 t} - \frac{p_1(0)\ _2^2 +\ \ +\ _1\ +\ _2\ \ _2 +}{\Omega_2(\Omega_1 - \Omega_2)} e^{\Omega_2 t} \qquad (2.11)$$

$$p_2(t) = \frac{\lambda\nu H}{\Omega_1\Omega_2} + \frac{p_2(0)\ _1^2 +\ \ +\ _2\ +\ _1\ +\ _3\ \ _1 +}{\Omega_1(\Omega_1 - \Omega_2)} e^{\Omega_1 t} - \frac{p_2(0)\ _2^2 +\ \ +\ _2\ +\ _1\ +\ _3\ \ _2 +}{\Omega_2(\Omega_1 - \Omega_2)} e^{\Omega_2 t} \qquad (2.12)$$

$$p_3(t) = \frac{\lambda\mu H}{\Omega_1\Omega_2} + \frac{p_3(0)\ _1^2 +\ \ +\ _3\ +\ _2\ \ _1 +}{\Omega_1(\Omega_1 - \Omega_2)} e^{\Omega_1 t} -$$

$$- \frac{p_3(0) \quad {}^2_2 + \quad + \quad {}_3 \quad + \quad {}_2 \quad {}_2 +}{\Omega_2(\Omega_1 - \Omega_2)} e^{\Omega_2 t} \quad (2.13)$$

These formulas will be used for determining of the age of artistic paint.

3. MEASUREMENTS DETERMINING AGE OF ARTISTIC PAINT

Determining of age of artistic paint requires series of mesurements of H_2O conteints. It should be pointed out that we do not know when was the initial momentum $t = 0$, since we do not know when the painting was finished. Consequentely, initial concentrations $p_1(0), p_2(0)$ and $p_3(0)$ are unknown. There is a posibility to determine initial concentration of H_2O molecules in the paint using computer scheme of paint distribution of paints. With help of this sheme we can reproduce paints of investigated artistic object and measure its humidity. It could be equal to initial concentration $p_1(0)$. Concerning measurements we must remember that the artistic paint must not be damaged, which means that no maesurements should be done on the artistic paint. It also means that the formula (2.11) will not be used. Measurements of humidity percentage of wider environment are not recommended due to the possible fluctuations of humudity in wider area (rain, snow, wind etc.).

On the bases of above reasoning it remains to measure H_2O contents in different moments in time in the room where the artistic paint is located. The humidity fluctuations in the room are very rare. Besides, the paint is in direct contact with air of the room (see Markov's graph). This direct contact gives more perceptible changes of humidity. Since the wider environment and the paint are not in direct contact, the changes of humidity of wider environment $p_3(t)$ would be weak, and this requires longer time intervals between two consecutive measurements. The final conclusion from preceding discussion is that all measurements are related to determining the concentrations $p_2(t)$.

The first measurement concetration p_2 gives $p_2(T)$, where T is the age of artistic paint in the moment of measurement. This concentration will be denoted with B_1.

On the basis of the formula (2.12), writen for $t = T$ we get the following expression formula:

$$R = \frac{B_1 - \Phi(x,y,T,B_0) - F(x,y,T,z,H)}{2\sinh yT} e^{xT} \circ \quad f(x,y,z,T,H,B_0) \quad (3.14)$$

where

$$B_7 = F(x,y,T+6t,z,H) + \Phi(x,y,T+6t,B_0) + \\ + \left[2e^{-x(T+6t)} \sinh(T+6t)\right] f(x,y,z,T+6t,H,B_0)$$

$$\chi = \frac{2\mu + v + \lambda}{2}, \quad y = \frac{1}{2}\sqrt{4\mu^2} + v^2 + \lambda^2 - 2v\lambda$$

$$z = v\lambda, \quad B_0 = p_2(0). \quad B_1 = p_2(T) \quad (3.15)$$

The functions Φ and F, figuring in (3.14) are given by:

$$\Phi(x,y,T,B_0) = B_0 \frac{y\cosh yT - x\sinh yT}{y} e^{-xT} \quad (3.16)$$

$$F(x,y,T,z,H) = \left[\frac{1}{x^2 - y^2} - \frac{x\sinh yT + y\cosh yT}{y(x^2 - y^2)} e^{-xT}\right] zH \quad (3.17)$$

The time unit in the formula (3.14) is one year. There appear six unknown values in (3.14): *x, y, z, T, H* and B_0. To determine these unknown parameters, we must carry out six measurements of concentration $p_2(t)$. The interval τ between two consecutive measurements can be taken to be one month, or half a month. In the first case $\tau = 1/12$ and in the second case $\tau = 1/24$. The first of these measurement must be done a month or half a month after the first measurement which has got value $B_1 = p_2(t)$.

The values of concentration obtained in moments $T+\tau$, $T+2\tau$, . . . , $T+6\tau$, will be denoted by B_2, B_3, ..., B_7, respectively. So we obtain the following system of the equations:

$$B_2 = F(x,y,T+t,z,H) + \Phi(x,y,T+t,B_0 + \\ + \left[2e^{-x(T+t)} \sinh(T+t)\right] f(x,y,z,T+t,H,B_0$$

$$B_3 = F(x,y,T+2t,z,H) + \Phi(x,y,T+2t,B_0) + \\ + \left[2e^{-x(T+2t)} \sinh(T+2t)\right] f(x,y,z,T+2t,H,B_0)$$

$$B_4 = F(x,y,T+3t,z,H) + \Phi(x,y,T+3t,B_0) + \\ + \left[2e^{-x(T+3t)} \sinh(T+3t)\right] f(x,y,z,T+3t,H,B_0)$$

$$B_5 = F(x,y,T+4t,z,H) + \Phi(x,y,T+4t,B_0) + \\ + \left[2e^{-x(T+4t)} \sinh(T+4t)\right] f(x,y,z,T+4t,H,B_0)$$

$$B_6 = F(x,y,T+5t,z,H) + \Phi(x,y,T+5t,B_0) + \\ + \left[2e^{-x(T+5t)} \sinh(T+5t)\right] f(x,y,z,T+5t,H,B_0) \quad (3.18)$$

Besides, in order to find the age of the paint *T,* which is the main goal of our analysis, we must find the distribution frequencies μ, ν and λ. These frequencies cannot be calculated directly from the formulas (3.18). They can be determined with the help of the values of *x, y* and *z* which are included into (3.18). Knowing *x, y* and *z,* we can find μ, ν and λ from the relations (3.15).

The solving of the system of equations (3.18), requires the use of numerical methods. The same requires the solving of the system (3.15).

Finishing this section we quote the following illustrative example.

For: $\tau = 1/24$; $B_1 = 2.7$; $B_2 = 2.7002$; $B_3 = 2.7005$;
$B_4 = 2.7007$; $B_5 = 2.70085$; *(3.19)*
$B_6 = 2.70095$; B_7=2.701;
we obtained:
$T = 65.25$ years; $H = 10$; $B_0 = 1.93$;
$x = 0.12547$; $y = 0.005966$; $z = 0.000047$ *(3.20)*

Substituting (3.20) into (3.15), we found the values for distribution frequencies:
λ= 0.011179; $\mu = 0.004847$; $\nu = 0.04221$.

It is seen that results obtained in this example are realistic.

4. CONCLUSION

The proposed method of determining the age of artistic paint has given satisfactory result: the age *T* can be determined without touch on the paint. The theory is based on really existing situation. Some idealizations are introduced by the fact that closed Markov's graph is used. This eliminated actually existing effect consisting of influence of walls, furniture etc. to the humidity of room. The main shortage of this approach is the moment of selling the artistic paint, since it occurs out of the room included in our theory.

In quoted illustrative example only one set of six values *B* was used. In practice the more realistic result could be obtained with *n* sets of six values *B*. These *n* sets would be obtained by changing of intervals τ between two successive measurements. In this way we should obtain *n* sets of results of the type (3.20). The values given in (3.20) would be calculated as arithmetic means of *n* values or as expectable values of them.

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SAŽETAK

UTVRĐIVANJE STAROSTI UMETNIČKIH BOJA MERENJEM SADRŽAJA H_2O

Predložena je metoda određivanja starosti umetničkih boja. Ona se zasniva na upotrebi zatvorenih Markovljevih grafova sa tri ćelije. Merenja sadržaja molekula vode u okolini može da se urade samo za prostor u kojem se nalazi umetničko platno. To znači da je metoda nedestruktivna.

Ključne reči: *koncentracija vlage, zatvoreni Markovljev graf, starost umetničkih boja, distribucija frekvencija.*