MATH 481, SPRING 2021

PROJECT 2
DETECTING ART FORGERIES

TYRON TENTION

Abstract. We formulate a system of differential equations corresponding to evolution in time of a mixture of radioisotopes uranium-238, radium-226, lead-210, and their eventual conversions to lead-206 which is not radioactive. We explain how our analysis may be applied to detect a forged oil painting.

1. Introduction

In this article we explain a method of distinguishing between a genuine and forged oil painting through the analysis of the ratios of radium-226 and lead-210 isotopes. These isotopes are generally present in all lead-based oil paints. The model presented here is akin to the one historically used in the context of the Van Meegeren art forgeries. Van Meegeren was an infamous painter who in the mid 20th century was suspected of forging works of the more famous 17th century Dutch painter Jan Vermeer. In order to prosecute Van Meegeren, a group of scientists collaborated on a model much like the one in this article in order to date the works of Van Meegeren [1, 2].

In section 2 we derive a system of differential equations which describe the quantities of radium-226 and lead-210 as functions of time. Then in section 3 we connect this model back to concept of art forgeries as described above by looking at the ratio of lead-210 and radium-226 present at equilibrium in white lead, a common base to which pigments are added, used by artists for over 2000 years. This ratio will tell us directly about the age of a painting.

2. The mathematical model

A radioactive material, such as uranium-238 (chemical symbol ^{238}U), decays according to:

$$\frac{d}{dt}Q(t) = -\lambda Q(t),$$

where $Q(t)$ is the amount of he radioactive material at time t and λ is the material's *decay rate* or *decay constant*. In this context, the "amount of material" refers to the number of atoms present in the sample.

The half life can be defined as the amount of time required for the number of atoms present at some initial time to decrease to exactly half that amount. This will be denoted τ, which is not to be confused with the lifetime $1/\lambda$. To derive the half life we must begin with exponential decay, $\frac{d}{dt}Q = -\lambda Q$. By separation of variables we get $\frac{dQ}{Q} = -\lambda dt$, which can be integrated to yield $ln(Q) = -\lambda t + C$.

Date: March 8, 2021.

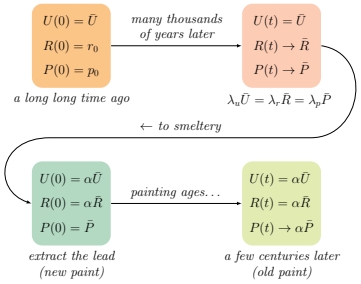

FIGURE 1. The starting amount of material approaches an equilibrium amount, with the uranium-238 content essentially remaining constant. Once the lead ore is processed and a new equilibrium is reached, we can use the new equilibrium relationship between the amounts lead-210 and radium-226 present to obtain the ratio, $\rho(t)$, of the amounts.

Our initial condition is that at time $t = 0, Q(0) = q_0$. We thus arrive at the familiar equation for *exponential decay*:

$$Q(t) = q_0 e^{-\lambda t}. \tag{1}$$

To determine the half life of a a radioactive atom, we simply set $Q(t) = \frac{1}{2}q_0$. Thus, by cancellation of the q_0's and the use of log rules, we arrive at

$$\tau = \frac{ln(2)}{\lambda}, \tag{2}$$

which allows us to calculate the *decay rate* given the half life for the radioactive atoms in question.

Uranium decays according to what is referred to as the "Uranium Series," in which uranium-238 decays into the non-radioactive element lead-206 via a series of α - and β - decays. This series of decays essentially changes the nucleus of the starting uranium, converting it into successively new elements, two of which are the radioactive atoms radium-226 and lead-210 that are found in white lead [1, 3]. The lead-210 eventually converts into the non-radioactive element lead-206.

The half lives of uranium-238, radium-226, and lead-210 are approximately 4.5 billion years, 1600 years, and 22 years, respectively. We can then easily calculate the decay rate by using equation (2) and rearranging to solve for λ. We obtain:

$$\lambda_u = 1.54 \times 10^{-10}$$
$$\lambda_r = 4.33 \times 10^{-4}$$
$$\lambda_p = 3.15 \times 10^{-2}.$$

As is evident by the excessively small value for the decay rate for uranium-238, we can essentially treat the amount of material present at any time to be constant.

The system of differential equations for the eventual production of lead-210 can be visualized for U $\to$ R $\to$ P, where we notice that the quantity U "disappears" to form radium, which in turn converts to P. However, since U-238 has such a large half life, its value within the range of a few thousand years can effectively be treated as a constant and its value at any time can be set equal to its equilibrium value,

$\bar{U}$. Hence:

$$\frac{dR}{dt} = -\lambda_r R + \lambda \bar{U},\ R(0) = R_0$$
$$\frac{dP}{dt} = -\lambda_p P + \lambda_r R,\ P(0) = P_0.$$

Using MAPLE, the solutions to this system after simplifying is given by

$$R(t) = -\frac{\left(\lambda_u \bar{U} - \lambda_r r_0\right) \mathrm{e}^{-\lambda_r t}}{\lambda_r} + \frac{\lambda_u \bar{U}}{\lambda_r}$$
$$P(t) = -\frac{\left(\lambda_u \bar{U} - \lambda_r r_0\right) \mathrm{e}^{-\lambda_r t^2}}{\lambda_p - \lambda_r} + \frac{\left(\lambda_r \lambda_u \bar{U} + \lambda_p^2 p_0 - \lambda_p p_0 \lambda_r - r_0 \lambda_p \lambda_r\right) \mathrm{e}^{-\lambda_p t}}{\left(\lambda_p - \lambda_r\right) \lambda_p} + \frac{\lambda_u \bar{U}}{\lambda_p}.$$

Now, by taking the limit as $t \to \infty$, we achieve the equilibrium values of radium-226 and lead-210 achieved after some few thousand years:

$$\bar{R} = \frac{\lambda_u \bar{U}}{\lambda_r}$$
$$\bar{P} = \frac{\lambda_u \bar{U}}{\lambda_p}.$$

Given that the amount of uranium present at any time can effectively be treated as constant, we can see from the above system that the equilibrium amounts $\bar{R}$ and $\bar{P}$ are related to the amount of uranium, $\bar{U}$, according to

$$\lambda_u \bar{U} = \lambda_r \bar{R} = \lambda_p \bar{P},$$

or equivalently,

$$\frac{\bar{U}}{\tau_u} = \frac{\bar{R}}{\tau_r} = \frac{\bar{P}}{\tau_p}, \tag{3}$$

where τ_u, τ_r, and τ_p are the half lives of ^{238}U, ^{226}Ra, and ^{210}Pb, respectively. Finally, We can take the ratio $\bar{P}/\bar{R}$, which yields

$$\frac{\lambda_r}{\lambda_p} = \frac{\tau_p}{\tau_r}. \tag{4}$$

3. Detecting A Forgery

Consider lead ore that has been in an undisturbed state for many thousands of years. Then the amounts of ^{238}U, ^{226}Ra, and ^{210}Pb will be interrelated as in the equilibrium equations (3).

The ore is taken to the smeltery to extract its lead. Essentially all of the lead-210 and lead-206 is recovered but most of the uranium and radium goes out as waste. Thus the equilibrium among ^{238}U, ^{226}Ra, and ^{210}Pb in the resulting product is lost.

Let's say that only a fraction α of the uranium and radium remains in the processed lead. For numerical experiments take $\alpha = 10^{-4}$. Now the system of equations becomes

$$\frac{dR}{dt} = -\lambda_r R + \alpha \lambda \bar{U},\ R(0) = \frac{\alpha \lambda_u \bar{U}}{\lambda_r}$$
$$\frac{dP}{dt} = -\lambda_p P + \lambda_r R,\ P(0) = \frac{\lambda_u \bar{U}}{\lambda_p}.$$

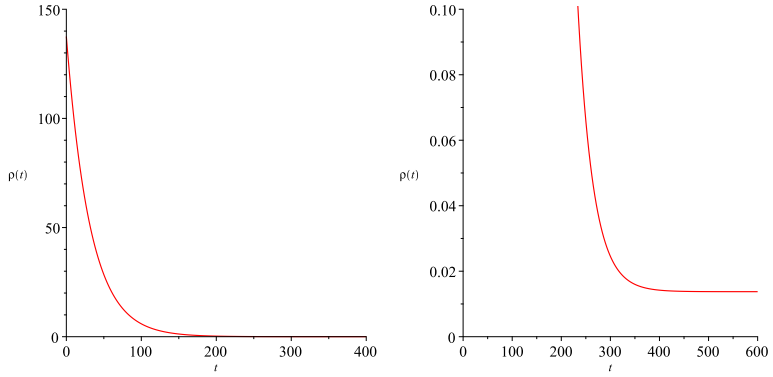

FIGURE 2. The first graph shows the overall progression of $\rho(t)$ over a period of 300+ years, whereas the second graph is meant to demonstrate the convergence of $\rho(t)$ to the value of $\bar{P}/\bar{R}$.

The initial conditions are based on the assumption that only some fraction α of the original uranium content is present in the paint. Now upon solving and factoring in MAPLE yields:

$$R(t) = \frac{\alpha\lambda_u\bar{U}}{\lambda_r} \tag{5}$$

$$P(t) = -\frac{\bar{U}\lambda_u(\alpha-1)\mathrm{e}^{-\lambda_p t}}{\lambda_p} + \frac{\alpha\lambda_u\bar{U}}{\lambda_p}.$$

We can then define $\rho(t)$ to be the ratio of $P(t)/R(t)$:

$$\rho(t) = -\frac{(\alpha-1)\lambda_r e^{-\lambda_p t}}{\lambda_p\alpha} + \frac{\lambda_r}{\lambda_p}, \tag{6}$$

where we can express $\rho(t)$ using our parameters to obtain

$$\rho(t) = 137.4862500\mathrm{e}^{-\frac{\ln(2)t}{22}} + \frac{11}{800},$$

which is graphed in Figure 2. Now, if we take the limit as $t \to \infty$, the exponential term tends to 0 and we obtain the same ratio as in (4) for the ratio of the amount of lead-210 and radium-226 present at equilibrium:

$$\rho = \frac{\bar{P}}{\bar{R}} = \frac{\lambda_r}{\lambda_p} = \frac{11}{800} = 0.01375,$$

although in the graphs above it is quite clear that this equilibrium value is reached after approximately 300 years have passed. It is important to note that even in the processed material once equilibrium has reached the ratio of lead-210 to radium-226 approaches the same value as in the unprocessed ore.

In the context of art forgeries, this tells us that after a few hundred years or so, once the concentrations of all radioactive compounds have reached equilibrium, the ratio of the number of atoms present at any time reaches the inverse ratio of their decay rates, and we get the value of $\rho(t)$ above. Hence, after a long time, the value of $\rho(t)$ approaches a value effectively close to zero. However, if the value of $\rho(t)$

is much higher, meaning the ratio of lead-210 to radium-226 present in the paint is quite large, then the isotopes are not in equilibrium. This relationship directly tells us about how old the painting is. The newer the painting is, the more lead-210 is present since it has not all decayed within its 22 year half life. It the painting is much older, such as the paintings of Jan Vermeer, then the concentrations of radioactive isotopes have reached equilibrium.

References

[1] Martin Braun. *Differential equations and their applications*. 2nd ed. An introduction to applied mathematics; Applied Mathematical Sciences, Vol. 15. Springer-Verlag, 1978.

[2] Wikipedia. *Johannes Vermeer*. Feb. 2019. URL: http://en.wikipedia.org/wiki/Johannes_Vermeer.

[3] Wikipedia. *Uranium-238*. Feb. 2019. URL: http://en.wikipedia.org/wiki/Uranium-238.

Department of Mathematics and Statistics, UMBC
Email address: tention1@umbc.edu