

DETERMINATION OF THE STABILITY OF OSMIUM(VI) HEXACHLORIDE ICP-OES STANDARDS IN HCl ACID MATRIX

Trevor T. Chiweshe^{*}, Abdon Atangana and Lore-Mari Deysel

Institute for Groundwater Studies, University of the Free State, Nelson Mandela Drive,
Bloemfontein, 9300, South Africa

(Received April 11, 2019; Revised October 4, 2019; Accepted January 21, 2020)

ABSTRACT. The ideal HCl concentration used in stabilizing osmium standards was investigated in this study. Additionally, mathematical models were tested to predict the decomposition rate of osmium standards at room temperature. Osmium(IV) hexachloride stock solutions stabilized in 7 and 15% HCl were used to assess the decomposition rate using ICP-OES. Several sets of calibration standards were prepared from the original stock solutions. The first calibration set was prepared with no additional HCl added to the final solutions and other sets with a total HCl acid concentration of 0.2, 0.4, 0.6, 1.0 and 1.5% v/v. Emission intensities were measured at 0, 24, 48, 72 and 96 hours. Standards with no additional HCl acid added kept at room temperature showed increase in emission intensities after 24 hours. These changes in emission intensities indicated chemical instability of osmium standards at low acid concentration levels. Standards stabilized in 1.0–1.5% HCl and refrigerated below 10 °C showed consistent emission intensities and had a shelf life of up to 48 and 72 hours, respectively. Four mathematical models were tested to determine the decomposition rate of the osmium standard. The first used rate of change concept and the second a stochastic approach. Both failed to capture osmium decay. The third was based on non-local operators with power law kernel and was able to capture the decay at earlier, but not later stages. The fourth, based on non-local operators with non-singular kernel was able to capture earlier and later decay due to its crossover properties in waiting time distribution.

KEY WORDS: Osmium stability, Osmium(IV) hexachloride, Hydrochloric acid matrix, Osmium emission intensities and nonlocal differential operators

INTRODUCTION

Amongst the platinum group elements (PGE), osmium is the least abundant stable element (50 parts per trillion) in the Earth's crust [1]. Osmium is mostly found in nature combined with iridium and other trace amounts of PGE in copper and nickel ores. The most common osmium ores are osmiridium (osmium rich) and iridosmium (iridium rich), which contains between 17–80% of osmium. In hydrometallurgy, osmium is recovered as osmium tetroxide from other PGE through distillation [2]. However, there are few applications of osmium tetroxide due to its volatility and toxicity [3]. Pure osmium is often alloyed with other PGE to increase tensional strength and is used in making pacemakers, heart valves [4], fountain pen tips, instrument pivots and electrical contacts [5].

Analysis of osmium using spectrometric techniques is not only complicated by its low concentrations, but by the formation of volatile compounds such as OsO₄ in aqueous solutions [6, 7]. Prevailing techniques for osmium analysis involves the use of spectrophotometric techniques, which often converts the different osmium species into one oxidation state or chemical form to avoid possible losses. In spectrometric analysis, osmium(IV) hexachloride is commonly used as a calibration standard [8]. Solutions containing osmium(IV) hexachloride in HCl acidic medium have been reported to undergo various chemical reactions in aqueous solutions, which include hydrolysis, disproportionation and aquatation [9]. Some of the anionic compounds formed in acidic solutions include [OsCl₅(H₂O)]⁻ that hydrolyses to [OsCl₄(H₂O)₂] and dimerizes to form [{(HO)Cl₄Os}₂O]⁴⁺, which depending on the conditions, can be oxidized

^{*}Corresponding author. E-mail: chiweshetrevor@gmail.com

This work is licensed under the Creative Commons Attribution 4.0 International License

to form OsO₄ (volatile compound) [10]. The formation of OsO₄ complicates the accurate determination of osmium and often requires standardization to avoid errors. The use of osmium(IV) hexachloride as a calibration standard in spectrometric techniques has been in the spotlight for a number of reasons, which includes its instability in aqueous solutions and its ability to easily form OsO₄. Exposure to light and high temperatures were amongst some of the common cited causes of instability in osmium calibration standard solutions [11]. The influence of scattered light on osmium(IV) hexachloride solutions has also been reported to result in the formation of a black-coloured precipitate (OsO₂·2H₂O) [12, 13]. Results from our previous studies also confirm the development of black stains on the stoppers of volumetric flasks [14]. The use of oxidizing agents such as H₂SO₄ and HNO₃ are also confirmed to promote the formation of OsO₄. Osmium standards stabilized in HCl acid matrix were shown to be more stable compared to other acids from the same group (HF, HBr and HI).

Research from our previous study shows inconsistent osmium recoveries due to the instabilities caused by the osmium calibration standards. Direct sunlight exposure was amongst some of the factors that were determined to affect the stability of osmium standards. The problem with the instabilities was circumvented by establishing an alternative osmium standard Cs₂[OsO₂(CN)₄], which was stable [13]. The continued use of osmium(IV) hexachloride prompted further research on the ideal factors needed to stabilize this calibration standard. Ammonium hexachloroosmate(IV) is the main compound used in the commercial preparation of osmium standards. Different acid concentrations (5–20%) of preferably hydrochloric acid are used for stabilization. However, discrepancies in the HCl acid concentrations in the osmium standards and uncertainties of the ideal acid concentration to ensure a longer shelf life remain an issue, which was investigated in this study. Different mathematical models were tested to predict the decomposition rate and shelf life of osmium standards. It is important to note that these mathematical models use differential and integral operators [15–17]. One can find in literature three different types of differential operators including differential operators with power law kernel, such can be used only if the observed real world problem follows the power law process. Differential operators with exponential decay law can be used when dealing with problems following fading memory process and with crossover properties. These last one are very useful when modelling real world problem following two different laws for instance power law and exponential decay law.

EXPERIMENTAL

Reagents and glassware

Two separate bottles of osmium standards, ammonium hexachloroosmate(IV) (NH₄)₂[Os(Cl)₆] (100 mL; 1 000 mg/L) stabilized in 7% v/v (*Std 1*) and 15% v/v (*Std 2*) HCl acid matrix were purchased from different chemical suppliers. Schott Duran beakers and Blaubrand grade (A) volumetric flasks were used for all chemical analyses.

Instrumentation

Shimadzu ICPS-7510 ICP-OES spectrometer with the torch vertically oriented (radial viewing plasma) was used for osmium analysis. A profile measurement programme within the ICP instrument was used to examine any emission intensity changes during the measurement. Rinsing time for osmium solutions was determined using a blank solution by monitoring the disappearance of the osmium peak. Selected measurement conditions for osmium analysis (Table 1) were used in all experimental measurements.

Table 1. ICP-OES selected operating conditions for osmium analysis.

Parameter	Condition
RF power	1.2 kW
Coolant gas flow rate	14.0 L/min
Plasma gas flow rate	1.2 L/min
Carrier gas flow rate	0.7 L/min
Sample uptake method	Peristaltic pump
Rinsing time	2.3 min
Type of spray chamber	Glass cyclonic
Type of nebulizer	Concentric
Injector tube diameter	3.0 mm
Wavelength	228.226 nm

Preliminary analysis of the two original osmium standards obtained from different suppliers

Two similar sets of osmium calibration standards solutions were prepared by pipetting aliquots of the original osmium standard solution $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ (*Std 1* and *Std 2*) using a calibrated 'Transferpette' micro-pipette into separate volumetric flasks (100.0 mL). The solutions were diluted to the mark using deionised water to yield concentrations between 0.5–10.0 mg/L (working range). No additional HCl was added into the standards. The solutions were homogenised and immediately analysed for the osmium emission intensities using the selected ICP conditions (Table 1). The average emission intensities of the calibration standards were recorded after every 24 hours (Figure 1).

Analysis of the osmium emission intensities of calibration standards prepared with varying amounts of HCl acid

Two sets of osmium calibration standards $(\text{NH}_4)_2[\text{Os}(\text{Cl})_6]$ (1,000 mg/L) with a working range of 0.5–10.0 mg/L were prepared by varying the HCl acid concentrations in each set (0.2, 0.4, 0.6, 1.0 and 1.5% v/v). All standards were homogenised. One set was left at room temperature and the other set was kept in a refrigerator at below 10 °C. The emission intensities of the osmium solutions were measured using the selected ICP conditions (Table 1) at 0 hours and then at 24 hour intervals thereafter. Changes in the slope of the calibration curves for standards at room temperature and refrigerated standards are reported in Figure 2 and Table 2.

Table 2. Determination of changes in calibration slope (sensitivity) with increase in HCl acid matrix of standards kept in a refrigerator below 10 °C.

Osmium calibration standards	HCl acid concentration (% v/v)	Sensitivity of the calibration curve				
		0 Hour	24 Hours	48 Hours	72 Hours	96 Hours
1	0.2	0.1522	0.1524	0.1526	0.1531	0.1542
2	0.4	0.1522	0.1523	0.1525	0.1528	0.1533
3	0.6	0.1522	0.1522	0.1523	0.1527	0.1530
4	1.0	0.1522	0.1522	0.1522	0.1523	0.1525
5	1.5	0.1522	0.1522	0.1522	0.1522	0.1522

RESULTS AND DISCUSSION

Analysis of the differences in osmium emission intensities and sensitivity drifts of the osmium standards OsCl_6^{2-}

Preliminary analysis of the two original standards used to prepare the working calibration standards showed variances in the osmium emission intensities. A repeat of this experimental

analysis revealed the same results which prompted further investigations. Slightly elevated osmium emission intensities were observed in calibration standards prepared from *Std 1* compared to those prepared from *Std 2* stock solutions. Graphical presentation of the calibration curve (Figure 1) showed an excellent linearity of both calibration curves (regression coefficient (R^2) of 0.9999) with different calibration gradients ($m = 0.1548$ and 0.1451 for *Std 1* and *Std 2*, respectively). These differences in the calibration gradient were unusual and pointed to the possibility of instrumental drifts which are a common cause of errors in analytical measurements.

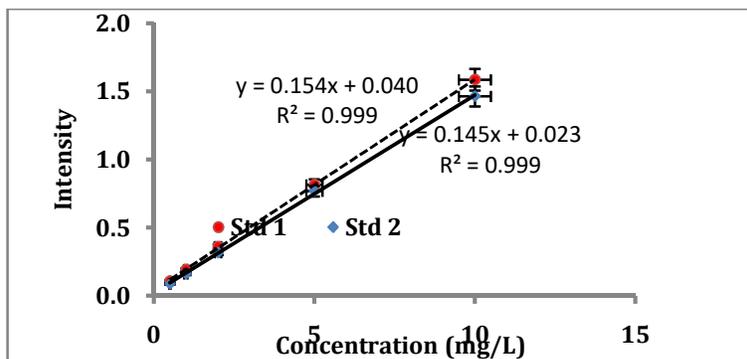


Figure 1. Differences in the calibration curves for osmium standards prepared from two different osmium standards, OsCl_6^{2-} (*Std 1* and *Std 2*).

Analysis into the possibilities of instrumental drift was performed by probing the ICP tubing for probable systematic errors of ten caused by the adsorption of osmium on the surface of the tubes. The analysis results showed that increasing the rinsing time (2.3 min) ensured a complete removal of trace amounts of osmium. Repeated measurements using the selected ICP measurement conditions (Table 1) showed consistent results which eliminated the possibility of instrumental drift as source of error.

The upward shift (sensitivity gain) as observed in Figure 2 was determined to be the result of the increase in osmium emission intensities. The causes of these emission intensities are a major concern and indications pointed to the possibilities of chemical instabilities caused by differences in the acid concentrations (7% and 15% v/v HCl) used for stabilization. Analysis of the calibration curves shows inconsistent drifts of the calibration plots from 0.1904 to 0.7199, which increased significantly with time (0-96 hours). The results also showed a rapid calibration shift between 24 and 72 hours, which suggests a rapid chemical change occurring within the standards.

The appearance of the black stains as seen on the volumetric flasks stoppers was a clear indication of the chemical instability occurring within the standard solutions. The stains were similar to those observed in our previous study [14] and could not be washed using either mineral acids or organic solvents. The presence of the black stain on the volumetric flasks stoppers pointed to the liberation of a gas from the standards. According to literature, the decomposition of OsCl_6^{2-} (standard) into OsO_4 occurs according to Equation 1 and is highly influenced by pH, light and temperature [11, 18, 19].



The possible cause for the increase in osmium emission intensities was the formation of OsO_4 in the calibration standards. The black stains on the volumetric flasks stoppers also provided

evidence of the gas formation (OsO_4 , 1.31 kPa vapour pressure at 25 °C) [20]. Several authors also attribute this gain in osmium emission intensities to the presence of OsO_4 [21]. The study by Bazan *et al.* [22, 23] also confirms the effects of OsO_4 using ICP-OES. These findings together with our experimental observations clearly suggest that OsO_4 contributes significantly to the increase in emission intensities which results in the calibration curves drifts.

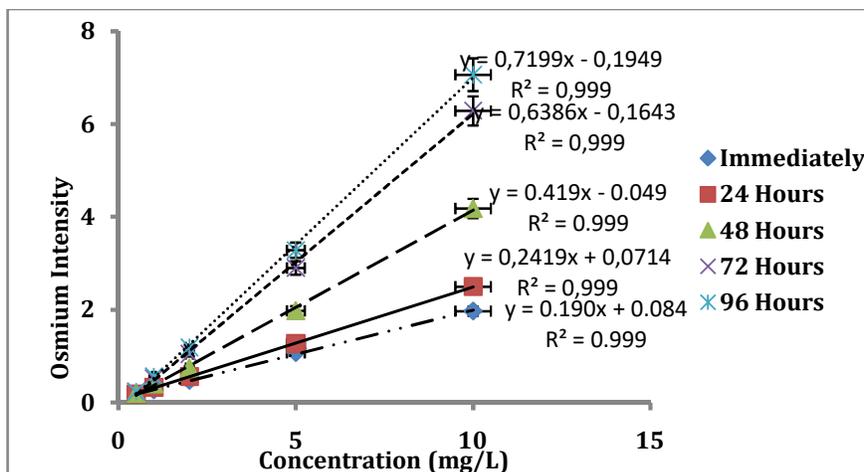


Figure 2. The upward shift of the osmium calibration curve (sensitivity gain) due to increase in the emission intensities.

It was alluded that the magnitude of the drift in the calibration curves (Figure 2) was arguably proportional to the amount of OsO_4 formed. The sharp calibration drift observed between 24 and 72 hours was also presumed to be the result of the rapid decomposition of the standard (OsCl_6^{2-}) to OsO_4 . However, the absence of calibration drifts in the first 24 hours suggests the stability of the standards solution (no OsO_4 formation) at room temperature. An experimental analysis to confirm the changes in concentrations of the calibration standards showed a decrease in osmium concentration over time (Figure 3). This decrease in concentration was attributed to the loss of osmium as OsO_4 .

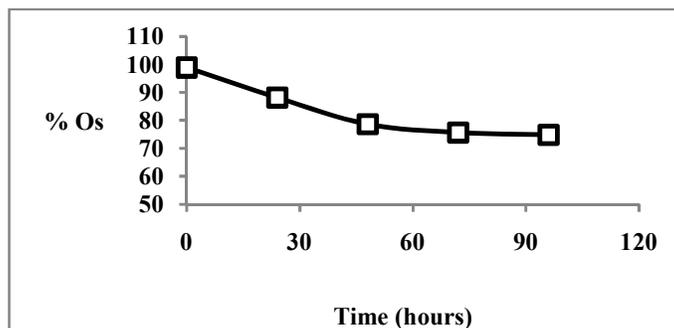


Figure 3. Decrease of osmium concentration as the result of the instability of the osmium calibration standard (OsCl_6^{2-}).

Determination of the stability of osmium standards by increasing HCl acid concentrations

The effects of acid concentration on the stability of osmium standards were monitored by varying the HCl acid concentration in each calibration set. Results of this investigation performed at room temperature showed an inverse correlation between the osmium emission intensities and the acid concentration. Significant sensitivity drifts were observed for standards stabilized with low acid concentrations (0.2–1.0% v/v) compared to those with high acid concentrations (1.0–1.5% v/v). At higher HCl acid concentrations (1.5% v/v), stable osmium emission intensities were recorded and no sensitivity drifts were observed. These results confirmed the influence of acid concentration towards the stability of osmium standards. Osmium standards with little or no HCl acid as a stabilizer left at room temperature were prone to decomposition as evidenced by the sensitivity drifts. Calibration standards with HCl acid concentration of 1.5% v/v kept in a cool environment showed small calibration drifts, which implied a slow decomposition rate.

Statistical estimations of percentage error for osmium analysis with acid concentrations between 0.2–1.0% (Table 3) were performed. Calibration standards kept at room temperature revealed a statistical error of up to 0.59% for all experimental results obtained after 24 hours and 0.13% for refrigerated standards. The percentage errors for osmium analysis increased depending on the period of time the standards were stored. Calibration standards kept for 4 days at room temperature and in a refrigerator had percentage errors of 3.86% and 1.11%, respectively.

Table 3. Estimations of the percentage error in osmium calibration standards stabilized between 0.2–1.0% HCl acid.

Time (hours)	Room temperature		Refrigerated (below 10 °C)	
	Sensitivity	Error (± %)	Sensitivity	Error (± %)
0	0.1522	-	0.1522	-
24	0.1522 - 0.1531	0.59	0.1522 - 0.1524	0.13
48	0.1523 - 0.1537	0.92	0.1522 - 0.1526	0.26
72	0.1525 - 0.1547	1.44	0.1523 - 0.1531	0.53
96	0.1528 - 0.1587	3.86	0.1525 - 0.1542	1.11

Mathematical models

The experimental observation shows a decrease in the concentration of the osmium standard, OsCl_6^{2-} with time (Figure 3). The scientific question thus arises in this case is the issue of time where these calibration standards (OsCl_6^{2-}) can still be usable regardless of the acid concentration. To answer this question, we construct a mathematical model where we consider $C[t] = [\text{OsCl}_6^{2-}]$ as the concentration of the osmium standard (OsCl_6^{2-}) at any given time. To understand the change in time of this chemical process, we evaluate the rate of change of the concentration in time as:

$$\frac{dC[t]}{dt} = -TC[t] \quad (1)$$

The presence of temperature is motivated by the fact that the decay is a function of temperature. The exact solution on the above equation is given by:

$$C[t] = C[0]\exp[-Tt] \quad (2)$$

where $C[0]$ is the initial concentration of OsCl_6^{2-} . The model assumes that the temperature within the room is constant at any given time. To find the time at which the concentration $C[t]$ is not useful, we solve the following equation:

$$C_{exp} = C[0]\exp[Tt_{us}] \quad (3)$$

$$t_{us} = \frac{1}{T} \ln \left[\frac{C[0]}{C_{exp}} \right]$$

A practical approach model will consider temperature to change with time in the range $[T_{min}, T_{max}]$. The temperature (\hat{T}) can now be considered as a distribution.

$$\hat{T} = T_{mean} + \rho X_1 \quad (4)$$

where T_{mean} is the mean of temperature sample, ρ is a stochastic constant, X_1 is any distribution. The new equation is then given as:

$$\frac{dC[t]}{dt} = -\hat{T}C[t] \text{ with exact solution} \quad (5)$$

$$C[t] = C[0] \exp[-\hat{T}t] \quad (6)$$

We shall in addition note that the first two suggested models are based on the Markovian process, [24] which are known to be memory less and therefore they are not able to capture memory effect of the chemical process. A new concept was introduced and used intensively in many fields of science, technology and engineering; in the following section, we use this concept to describe the decay. If we assume that the waiting time distribution of the chemical process follows the power law, then the model takes the following form:

$$\frac{1}{\Gamma(1-\alpha)} \int_0^t \frac{dC[y]}{dy} (t-y)^{-\alpha} dy = -TC[t] \quad (7)$$

Using the Laplace transform, [20] we obtain the exact solution as:

$$C[t] = C[0] E_{\alpha}[-Tt^{\alpha}] \quad (8)$$

where $E_{\alpha}(-t^{\alpha})$ is the generalized Mittag-Leffler function given as:

$$E_{\alpha}[-t^{\alpha}] = \sum_{j=0}^{\infty} \frac{(-t)^{\alpha j}}{\Gamma(\alpha j + 1)} \quad (9)$$

The chemical process waiting substitution follows the exponential law and then the model takes the following form:

$$\frac{1}{(1-\alpha)} \int_0^t \frac{dC[y]}{dy} \exp\left[-\frac{\alpha}{(1-\alpha)}(t-y)\right] dy = -TC[t] \quad (10)$$

The exact solution is given as:

$$C[t] = C[0] \exp\left[-\frac{\alpha T t}{1-(1-\alpha)T}\right] \quad (11)$$

Finally, if the chemical process waiting time distribution follows at the same time, power law and exponential law [15-17] then the new model will be:

$$\frac{AB(\alpha)}{1-\alpha} \int_0^t \frac{dC[y]}{dy} E_{\alpha}\left[-\frac{\alpha}{1-\alpha}(t-y)^{\alpha}\right] dy = -TC[t] \quad (12)$$

$$AB(\alpha) = 1 - \alpha + \frac{\alpha}{\Gamma(\alpha)}$$

Using the Laplace transformation, the exact solution is given as:

$$C[t] = C[0] E_{\alpha}\left[-\frac{\alpha T t^{\alpha}}{AB(\alpha) - (1-\alpha)T}\right] \quad (13)$$

Based on the experimental results, we aim in this section to test the efficiency of each differential operators used to construct equation 1, 7 and 13. We consider in this simulation a

constant average temperature of approximately 25 °C and the initial concentration to be 100% $OsCl_6^{2-}$, the additional parameter alpha appearing in the two last equations is a representation of memory (taking into account the change in temperature, error done in the measurement and finally variation within the laboratory). The numerical simulation is presented in Figure 4 for the first mathematical model using the classical differential operator that is commonly used in chemistry.

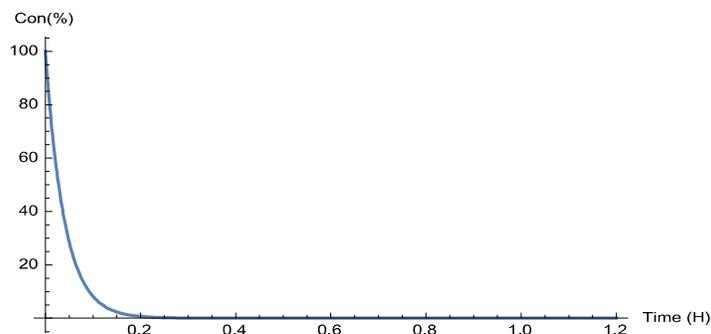


Figure 4. Model with classical differentiation.

Figure 5 shows the model based on the fractional differential operator with power law waiting time distribution and Figure 6 shows the model based on the differential operator with crossover in waiting time distribution. It is clear from the Figure 4 that the model with the classical differential operator cannot account accurately for the decay of osmium; the model cannot be used to predict the future behaviour of the chemical reaction neither for earlier nor later time. The model based on the differential operator with power law waiting time distribution (Figure 5), however, manages to capture the earlier but not later time decay. This is because the differential operator does not have crossover behaviour [15-17]. The model based on the differential operator with crossover in waiting time distribution provides us with a better understanding of the decay from earlier to later time and this is observed for smaller representation of the new alpha parameter.

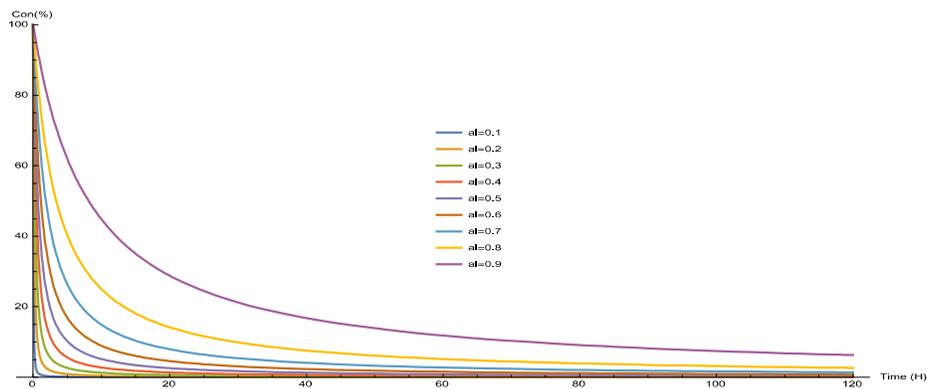


Figure 5. Model with power law waiting time distribution.

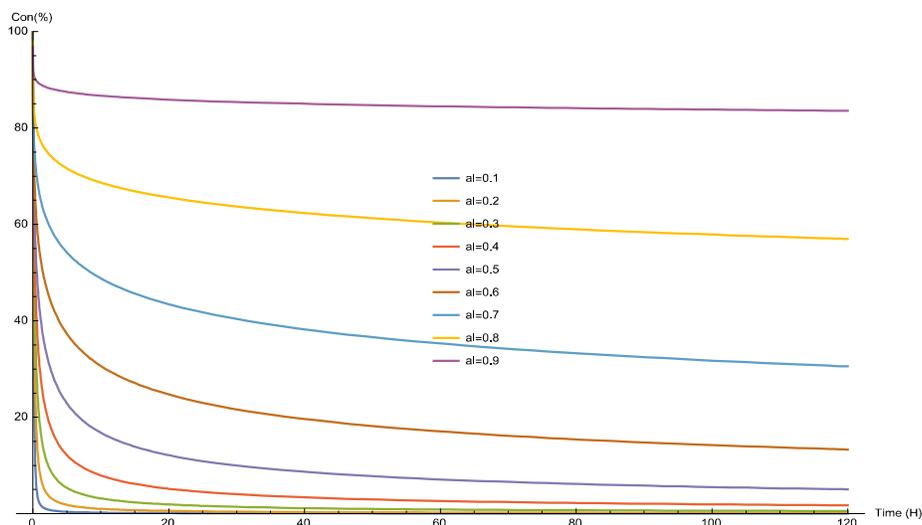


Figure 6. Model with crossover in waiting time distribution.

CONCLUSION

Results showed that variations in both temperature and acid matrix affected the shelf life of osmium calibration standards. Decomposition of the osmium standards (OsCl_6^{2-}) to OsO_4 occurred rapidly in solutions with low acid concentration ($> 1\%$) at room temperature ($25\text{ }^\circ\text{C}$). Osmium standard decomposition included the decrease in osmium concentration, which was due to the volatilization of OsO_4 . Calibration standards stabilized in higher acid concentrations (1.0–1.5% HCl), decomposed slowly at cooler temperatures when stored in a refrigerator. We proposed in this work a mathematical model, which is able to portray the decay of osmium at an average temperature. The decay could have been related to the power law, exponential law or Mittag-Leffler law. In order to verify which one was suitable, we investigated four partial differential equations with different differential operators. The Mittag-Leffler law was found to be suitable for such decay. This study will help chemists understand that the classical differentiation, although used intensively in the field of chemistry, has severe limitations that could hamper predictions. Therefore, a chemist could revert to modelling with non-local differentiation.

ACKNOWLEDGEMENT

The authors thank the Research Fund of the University of the Free State for financial support.

REFERENCES

1. Wedepohl, H.K. The composition of the continental crust. *Geochim. Cosmochim. Acta* **1995**, 59, 1217-1232.
2. Raleigh, G. The platinum metals. *Chem. Rev.* **1943**, 32, 277-372.
3. Griffith, W.P. Osmium tetroxide and its applications. *Platinum Metals Rev.* **1974**, 18, 94-96.
4. Griffith, W.P. Osmium and its compounds. *Q. Rev. Chem. Soc.* **1965**, 19, 254-273.

5. Cramer, S.D.; Covino, B.S. *ASM Handbook Corrosion: Materials*, Vol. 13B, ASM International: USA; **2005**; pp 1-704; ISBN 978-0-87170-707-9.
6. Tyutyunnik, O.A.; Varshal, G.M.; Koshcheeva, I.Y.; Roshchnina, I.A.; Myasoedova, G.V.; Shcherbinina, N.I.; Milovzorov, N.G.; Shumskaya, T.V. Determination of osmium by sorption-X-ray fluorescence technique. *J. Anal. Chem.* **2000**, *55*, 350-353.
7. Chiweshe, T.T.; Purcell, W.; Venter, J.A. Evaluation of different internal standards for precious metals. *Bull. Chem. Soc. Ethiop.* **2016**, *30*, 55-70.
8. Vrublevska, T.; Rydchuk, M.; Bonishko, O.; Mykhalyna, G. A simple titrimetric method for the determination of osmium(IV) in standard chloride solution and intermetallic alloys. *Mater. Sci.* **2010**, *46*, 399-407.
9. Losev, V.N.; Kudrina, Y.V.; Trofimchuk, A.K.; Komozin, P.N. Feature of the sorptive extraction of osmium in different oxidation states with silica gels chemically modified with mercapto and disulphide groups. *J. Anal. Chem.* **2004**, *59*, 546-551.
10. Moskvina, L.N.; Shmatko, A.G. Kinetics of the reactions of substitution of $[\text{OsCl}_6]^{2-}$ and $[\text{Os}(\text{H}_2\text{O})\text{Cl}_5]$ ligands in solutions of HCl. *Zh. Neorg. Khim.* **1988**, *33*, 1229-1234.
11. Bazan, J.M. Enhancement of osmium detection in inductively coupled plasma atomic emission spectrometry. *Anal. Chem.* **1987**, *59*, 1066-1069.
12. Khvostova, V.P.; Kadyrova, G.I.; Alimarin, I.P. Investigation of the state of osmium(IV) in solutions of hydrochloric acid. *Izv. Akad. Nauk. Ser. Khim.* **1977**, *11*, 2418-2422.
13. Kulprathipanja, S.; Hnatovich, D.J.; Treves, S. The hydrolysis and radiolysis of ^{191}Os hexachloroosmate(IV). *J. Inorg. Nucl. Chem.* **1977**, *39*, 933-935.
14. Chiweshe, T.T.; Purcell, W.; Venter, J.A. ICP-OES monitoring of the instability of $[\text{OsCl}_6]^{2-}$ and evaluation of $[\text{OsO}_2(\text{CN})_4]^{2-}$ as alternative standard for osmium quantification. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1054-1063.
15. Abro, K.A.; Khan, I.; Nisar, K.S. Novel technique of Atangana and Baleanu for heat dissipation in transmission line of electrical circuit. *Chaos, Solitons & Fractals* **2019**, *129*, 40-45.
16. Gómez-Aguilar, J.F.; Abro, K.A.; Kolebaje, O.; Yildirim, A. Chaos in a calcium oscillation model via Atangana-Baleanu operator with strong memory. *Eur. Phys. J. Plus* **2019**, *134*, 140-149.
17. Abro, K.A.; Gómez-Aguilar, J.F. A comparison of heat and mass transfer on a Walter's B fluid via Caputo-Fabrizio versus Atangana-Baleanu fractional derivatives using the Fox-H function. *Eur. Phys. J. Plus* **2019**, *134*, 101-112.
18. Taddia, M.; Lucano, C.; Juris, A. Analytical characterization of supramolecular species- Determination of ruthenium and osmium in dendrimers by electrothermal atomic adsorption spectrometry. *Anal. Chim. Acta* **1998**, *375*, 285-292.
19. Wiersman, J.H.; Lott, P.F. Spectrophotometric determination of osmium with thiocyanate. *Anal. Chem.* **1967**, *39*, 674-676.
20. Svorc, L.; Tomcik, P.; Durdiak, J.; Rievaj, M.; Bustin, D. Analytical methods for the detection of osmium tetroxide: A review, *Pol. J. Environ. Stud.* **2012**, *21*, 7-13.
21. Summerhays, K.D.; Lamothe, P.J.; Fries, T.L. Volatile species in inductively coupled plasma atomic emission spectroscopy; Implications for enhanced sensitivity. *Appl. Spectrosc.* **1983**, *37*, 25-28.
22. Russ, G.P.; Bazan, J.M.; Date, A.R. Osmium isotopic ratio measurements by inductively coupled plasma source mass spectrometry. *Anal. Chem.* **1987**, *59*, 984-989.
23. Bazan, J.M. Enhancement of osmium detection in inductively coupled plasma atomic emission spectrometry. *Anal. Chem.* **1987**, *59*, 1066-1069.
24. Mathai, A.M.; Haubold, H.J. *Special Functions for Applied Scientists*, Springer: New York; **2008**, 26, 10-78; ISBN 978 0387 758930.