



The Hydroquinone level and pH of the developer solution are based on the length of time of exposure to free air

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Abstract

Conventional radiography is still widely used in medical practice, characterized by chemical film processing. One crucial stage in chemical film processing is the film development stage. One of the main components of film developer solutions is hydroquinone. Oxidation affects hydroquinone levels and is related to the pH of the developer solution. This study aims to determine the effect of air oxidation on the pattern of changes in hydroquinone levels and the pH of the film developer solution. This experimental laboratory study consisted of 32 samples divided into eight groups. Hydroquinone levels were measured using HPLC instrument. Data were analyzed using the one-way ANOVA and Unpaired T-test ($\alpha=0.05$). The highest levels (hydroquinone = 594.75 and 256.5 ppm; pH = 11.85 and 10.75) were obtained in the group that was not exposed to free air, and the lowest (hydroquinone = 0.79 and 0.54 ppm; pH = 8.7 and 7.9) in the group that was exposed to free air for 30 days. There were significant differences in hydroquinone levels and pH of the developer solution based on the duration of oxidation in free air. There was a similar pattern of decrease in hydroquinone levels and the pH of the developer solution.

Keywords: Radiography film developer solutions, Hydroquinone, Oxidation, pH

Introduction

Radiographic examination is the main imaging modality and has an important role as the main support for the diagnosis of various diseases, treatment planning, and evaluation of treatment results [1]. Radiographic examinations are now widely available and easy to use, inexpensive, non-invasive, well-known among medical professionals, relatively harmless compared to other imaging modalities, and relatively quick to perform [2].

Although radiographic examinations have evolved towards digital radiography, conventional radiography is still widely used in various health care facilities. Conventional radiography is primarily characterized by chemically processed film. Chemical film processing involves several stages to produce a good and accurate image of the condition of a tissue or organ within the body. One crucial stage of chemical film processing is film development in a developer solution, other stages include rinsing, fixing, washing, and drying [2, 3].

In the film development stage, the film is processed in a developer solution which aims to reveal the latent image into a visible image on the film. The component in the developer solution which functions to form the latent image into a visible image on the film is the developer agent [4]. One of the main ingredients in the developer agent is hydroquinone (HQ). Previous research found a gradual decrease in hydroquinone depending on the length of time the developer solution was in contact with free air. A drastic decrease in hydroquinone levels occurred on the 30th day of measurement. The study also found differences in the pattern of hydroquinone reduction between the developer solution concentrations used (50% and 25%). The decrease in HQ levels in this study occurred due to the oxidation

process of the developer solution, and specifically the oxidation process of hydroquinone [5]. It is known that hydroquinone is a rapidly oxidizing agent in free air. Hydroquinone readily undergoes autooxidation within a few weeks. The effectiveness of hydroquinone decreases proportionally with the ease of autooxidation [6, 7].

The activity of the developer solution is influenced by oxidation which has an impact on the level of Hydroquinone, the temperature of the solution, the pH of the solution and the amount of film developed [4]. Hydroquinone in the developer solution is almost inactive and its ability will decrease if the pH of the solution is less than 9 [3], so that the developer solution becomes non-selective in distinguishing between silver halide (AgBr) exposed to x-rays and those that are not, so that the formation of latent shadows on the radiographic film cannot occur or is imperfect and produces non-diagnostic radiographs [8, 9].

Thus, the hydroquinone levels in the developer solution is related to the oxidation process, the pH of the developer solution, and of course, the initial concentration of the developer solution. This study aims to continue previous research by observing changes in pH and hydroquinone levels of two different developer solution concentrations based on the length of exposure to free air.

Methodology

This laboratory experimental study used a post-test only control group design. The study used 32 samples divided into 8 groups (4 groups for the 25% developer solution and 4 groups for the 50% developer solution), so that each group consisted of 4 samples. Group 1 for each concentration was the control group (exposed to free air for 0 days), group 2 for 7 days, group 3 for 14 days, and group 4 for 30 days.

The study was conducted at the Radiology Laboratory of the Faculty of Dentistry and the Analytical Chemistry Laboratory of the Faculty of Pharmacy, University of Jember. The film developer solution used was the Carestream GBX Developer Replenisher developer brand. The research samples were stored in open glass containers at room temperature for a time adjusted to the sample group. The samples were prepared by dissolving distilled water and filtered using a 0.2 µm millipore. Hydroquinone levels were measured using the HPLC (High-Performance Liquid Chromatography) method. A total of 20 µl of sample preparation was injected into the HPLC with a wavelength of 295 nm, a flow rate of 1.0 ml/min. The results of the

sample measurements in the chromatogram area, a hydroquinone standard injection was carried out on the HPLC to produce a standard curve to convert the results of the sample area into ppm units. Standard hydroquinone was injected at various levels, and two standard curve equations were obtained. Previously, the pH value was measured using a pH meter. The data obtained were analyzed using one-way ANOVA and T-test ($\alpha=0.05$).

Results

Hydroquinone levels were measured as in previous research [5]. The results of the research on hydroquinone levels are presented in the table below.

Table 1: Hydroquinone levels in developer solution

Sampel number	Group	Hydroquinone Levels (ppm)				
		length of time exposed to free air				
		0 days	7 days	14 days	30 days	Mean
A	1	271	6	1.95	0.5	69.86
	2	262	6.86	1.54	0.46	67.72
	3	239	7.1	1.36	0.58	62.01
	4	254	6.91	1.98	0.62	65.88
	Mean (SD)	256,5 (13,6)	6,71 (0,5)	1,70 (0,3)	0,54 (0,1)	
B	1	617	426	275	0.78	329.69
	2	599	455	252	0.74	326.69
	3	578	432	240	0.81	312.70
	4	585	460	270	0.86	328.97
	Mean (SD)	594,75 (17,2)	443,25 (16,7)	259,25 (16,19)	0,79 (0,0505)	

A= developer solution with a concentration of 25%

B= developer solution with a concentration of 50%

SD= Standart deviation

The data in Table 1 shows that for both developer solution concentrations, hydroquinone levels gradually decreased according to the length of exposure to free air. Hydroquinone levels were highest in the control group (0

days) and lowest in group 4 (30 days of exposure). In general, the concentration of hydroquinone in the 50% developer solution is higher than the 25% concentration in each group with the duration of exposure to free air.

Table 2: Hydroquinone levels in the developer solution are based on the length of time exposed to free air and the results of statistical tests

Group	Mean of Hydroquinone Levels (ppm)								
	A			B			C		
	Mean	SD	p	Mean	SD	p	Mean	SD	p
0 days	256,5	13,576	0,00	594,75	17,211	0,00	384,75	87,07	0,00
7 days	6,71	0,489		443,25	16,76		224,98	8,51	
14 days	1,70	0,306		259,25	16,194		130,48	8,25	
30 days	0,54	0,076		0,79	0,0505		0,67	0,06)	

p= Significance value of one-way Anova test

C= The combined value of the Hydroquinone levels of developer solutions from concentrations of 25% and 50%

The results of the one-way ANOVA statistical test (table 2) showed a significant difference ($p < \alpha$) in the hydroquinone levels in the developer solution between groups of time

exposed to free air, both at concentrations of 25%, 50% and the combined hydroquinone levels of the two concentrations.

Table 3: The level of hydroquinone in the developer solution exposed to free air based on the concentration

Sample number	Hydroquinone Levels (ppm)						p
	1	2	3	4	Mean	SD	
A	69,86	67,72	62,01	65,68	66,37	3,333	0,000
B	329,69	326,69	312,70	328,97	324,51	7,98	

p = Unpaired t-test (Sig)

Based on the results of the Unpaired T-test, a significant difference ($p < \alpha$) was found in the levels of Hydroquinone in the developer solution between concentrations of 25% and 50%.

Tabel 4: pH value of developer solution

Variable	pH Value							
	A				B			
Sample group	0 days	7 days	14 days	30 days	0 days	7 days	14 days	30 days
1	11	9.0	7.8	8.1	12	9.5	10	9.3
2	10.7	9.6	8.5	8	12.1	10.6	9.9	8.5
3	10.4	9.5	8.6	7.6	11.6	10.8	9.8	8.6
4	10.9	9.2	8.2	7.9	11.7	10.5	9.7	8.4
Mean	10,75	9,33	8,28	7,9	11,85	10,35	9,85	8,7
SD	0.26	0.28	0.36	0.22	0.24	058	0.13	0.41
p	0,000				0,000			

A= developer solution with a concentration of 25%

B= developer solution with a concentration of 50%

p= Significance value of one-way Anova test

The data in Table 4 shows that for both developer solution concentrations, the pH value decreased gradually with the duration of exposure to free air. The highest pH was in the control group (0 days) and the lowest in group 4 (30 days of exposure). In general, the pH of the 50% developer solution

was higher than that of the 25% concentration in each group with the duration of exposure to free air.

Based on the results of the one-way ANOVA test (table 2), a significant difference ($p = 0,000$) was found in the pH value in the developer solution between the groups of time exposed to free air

Tabel 5: The pH value of the developer solution exposed to open air for different periods of time based on the concentration of the solution

Group	Sampel	pH value				Mean (SD)	Unpaired T-test (Sig)
		1	2	3	4		
A		9.9	9.2	9.01	9.05	9.06 (0,097)	0.000
B		10.2	10.28	10.2	10.08	10.19 (0,083)	

A= developer solution with a concentration of 25%

B= developer solution with a concentration of 50%

Based on the results of the T-test, there was a significant difference ($p=0.000$) in the pH value of the developer solution between concentrations of 25% and 50%.

Radiographic film developer solutions have a usage limit, meaning that the film developer solution can only process a certain amount of film before its chemical composition degrades. The developer solution can weaken and the film will fail to develop properly, resulting in poor image quality on the radiograph. Radiographic film developer solutions generally contain two developing agents, the most commonly used being metol + hydroquinone or phenidone + hydroquinone. Hydroquinone ($C_6H_4(OH)_2$) plays an important role in being one of the developing agents in radiographic film developer solutions. Hydroquinone has high selectivity and produces high-contrast image density that is produced slowly^[10, 11].

High-Performance Liquid Chromatography (HPLC) is a separation technique, which can be applied to analyze compounds of different properties from the low up to very high molecular mass substances the^[12]. HPLC instruments are used to measure hydroquinone because of its fast analysis time, good separation power so that compounds can be analyzed selectively without being affected by the presence of other compounds, and sensitive to determine the levels of compounds in small concentrations.^[13] HPLC is a separation technique that has been widely accepted to analyze and purify certain compounds in a sample in several fields, including the pharmaceutical, environmental, biotechnology, polymer, and food industries. This method has the advantage of high separation power so that it will not give false negative results and can analyze compounds in small levels. The working principle of HPLC is the

separation of solutes by differences in the elution speed of solute-solute substances passing through a chromatographic column. The separation process occurs with the help of a liquid mobile phase pump flowing through the column to the detector^[12].

The research results showed a gradual decrease in hydroquinone levels depending on the length of time the developer solution was exposed to free air. This result can be explained by the hydroquinone undergoing oxidation due to exposure to free air. Hydroquinone is one type of chemical compound that falls into the phenol group. Phenol is a chemical compound that can be easily oxidized and undergo an evaporation process in the air or oxidizedm^[6] Oxidation is a chemical reaction involving removing electrons from a molecule, atom, or ion. Oxidation can be alternatively defined as the incorporation of a substance with oxygen. Oxidation and reduction must always occur together; such reactions are called oxidation-reduction or redox reactions^[14].

Oxidation is a chemical reaction involving the transfer of electrons from one substance to another. These reactions can cause changes in the chemical structure of substances, including changes in chemical bonds, functional groups, and physical and chemical properties of substances^[15]. Changes in the chemical structure of substances in the most common oxidation reactions are combination, decomposition, combustion, and displacement^[16] The chemical structure of hydroquinone undergoes decomposition when subjected to oxidation. A decomposition reaction is decomposing a compound into two or more components. Hydroquinone will become quinone by the chemical reaction $C_6H_6O_2 \rightarrow C_6H_4O_2 + 2H^+$. This oxidation can occur spontaneously or

with the help of oxidizing agents, such as oxygen, sulfur dioxide, or potassium permanganate [17].

Changes in chemical structure can affect the properties of substances, such as solubility, catalytic activity, thermal stability, toxicity, and reactivity. Changes in properties that occur in hydroquinone are solubility and reactivity. Changes in solubility occur due to changes in the chemical structure of hydroquinone. Hydroquinone has a more polar structure than quinone, which makes hydroquinone more soluble in water, while quinone is difficult to dissolve in water. Changes in reactivity occur due to changes in the chemical structure of hydroquinone. Quinones have carbonyl groups that are more reactive than hydroxyl groups, so quinones are more reactive to other substances than hydroquinones [16]. Changes in these properties can affect hydroquinone levels in solution [14].

Measuring hydroquinone levels at different developer concentrations showed different rates of hydroquinone reduction. The difference in the rate of decrease in Hydroquinone levels is based on different oxidation speeds of Hydroquinone. Factors that can affect the oxidation speed of Hydroquinone are the pH of the initial solution and the initial content of Hydroquinone [18]. Hydroquinone oxidation is faster under acid than in alkaline conditions [19]. In this study, the pH of the initial solution in Sample Group A with a developer liquid concentration of 25% was lower than in Sample Group B with a developer liquid concentration of 50%. The initial Hydroquinone levels in the two sample groups were also different, where the sample group with a 50% developer fluid concentration contained more Hydroquinone than the sample group with a liquid concentration of 25%. These two factors affect the speed of decreasing Hydroquinone levels in both sample groups.

Oxidation of hydroquinone in water can produce a byproduct, namely Hydrogen Peroxide. The chemical reaction is $C_6H_6O_2 + O_2 \rightarrow C_6H_4O_2 + H_2O_2$. Hydrogen Peroxide has acidic properties, and the developer solution tends to be alkaline. Excessive production of hydrogen peroxide will lead to a decrease in the quality of radiographic images [6]. This research uses liquid developers with the brand Carestream GBX Developer. According to the manufacturer, the recommendation for making developer solutions is to mix developer liquid and water in a ratio of 1:4 or equivalent to 25% developer solution. This study showed a drastic decrease in hydroquinone levels and a change in colour to brown within seven days with a developer fluid composition of 25%. It can lead to a decrease in developing ability—using a weak developer solution when processing film will reduce the quality of radiographic images. Therefore, the developer solution is recommended to be used in less than seven days.

Conclusions

There were significant differences in hydroquinone levels and the pH of the radiography film developer solution based on the duration of oxidation in free air. Hydroquinone levels and pH decrease with increasing oxidation time in free air for 7, 14 and 30 days. There was a similar pattern of decrease in hydroquinone levels and the pH of the radiography film developer solution.

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Conflicts of Interest

The authors declare that all authors have no conflicts of interest related to the work reported in this paper.

References

1. Supriyadi, Swasthi Prastyarini, Dentist Perceptions on Dental-Radiodiagnosis Using Smartphone: Crosssectional study, *J Int Dent Med Res*,2022;15(2):783-788.
2. Ansari MDI, Arfat M, Malik MMUD. Review Article Conventional Radiography- A Comparison with Computed Radiography (CR). *Journal of Xi'an Shiyou University, Natural Science Edition*,2022;18(9):338-344.
3. Whaites E, Drage N. *Essentials of Dental Radiography and Radiology*. 6th ed., Edinburgh, London, New York etc.: Churchill Livingstone, 2020, 561.
4. Mallya S, Lam E. *White and Pharoah's Oral Radiology Principles and Interpretation*. Elsevier Health Sciences, 2019.
5. Assary Aufa Wardhana R. Hydroquinone Levels in Radiographic Developer Solutions are Based on Concentration and Length of Time Oxidized in Free Air. *Dentistry & Dent Pract J*,2025;7(1):180094.
6. Nasehzadeh A, Khosravan A, Resa SH. Kinetics and Mechanism of Aerial Oxidation of Hydroquinone in A Developer Solution and Determination of Developer's Half-Life At 20 C. *J. Sci. I. R. Iran*,1995;6(1):32-37.
7. Banodkar PD, Banodkar KP. History of hydroquinone. *Indian J Dermatol Venereol Leprol*,2022;88:696-9.
8. Iannucci JM, Howerton, LJ. *Dental Radiography Principles and Techniques*. (5th edition). Elsevier Health Sciences, 2017.
9. Zusagka E, Sutanto H, and Arifin Z, the effect of increasing the pH of the developer solution by adding NaOH and Na₂CO₃ on the image density, *Youngster Physics Journal*,2014;3:203-208.
10. Niemiec, BA, Gawor J, Jekl V. *Practical Veterinary Dental Radiography*. CRC Press, 2017.
11. de Carvalho F, da Silveira M, Frazão M, de Santana S, dos Anjos Pontual M. Effects of developer exhaustion on DFL Contrast FV-58 and Kodak Insight dental films. *Dentomaxillofacial Radiology*,2011;40:358–61.
12. Jesu's Lozano-Sa'nchez, Isabel Borra's-Linares, Agnes Sass-Kiss and Antonio Segura-Carretero. Chapter 13: Chromatographic Technique: High-Performance Liquid Chromatography (HPLC). *Modern Techniques for Food Authentication*,2018:450-526.
13. Khairy MA, Hamad A, Hamed M, Locatelli M, Mansour FR, A stability indicating RP-HPLC-UV assay method for the simultaneous determination of hydroquinone, tretinoin, hydrocortisone, butylated hydroxytoluene and parabens in pharmaceutical creams. *Journal of Pharmaceutical and Biomedical Analysis*,2024;242:116021.
14. Atkins P, Jones L. *Chemical Principles: The Quest for Insight*. 5th ed. W H Freeman, 2009.
15. Chang R, Overby J. *Chemistry*. 14th ed. McGraw Hill, 2022.
16. McMurry J. *Organic Chemistry*. 10th ed. Rice University, 2023.

17. Atkins P, Paula J, Keeler J. Atkins Physical Chemistry. 11th ed. Oxford University Press, 2018.
18. Zhengting Zhang, Guiyun Yi, Peng Li, Xikui Wang, Xiaodong Wang, Chuanxiang Zhang, Yulong Zhang, Qi Sun. Electrochemical Oxidation of Hydroquinone Using Eu-doped PbO₂ Electrodes: Electrode Characterization, Influencing Factors and Degradation Pathways. Journal of Electroanalytical Chemistry, 2021; 895: 115493.
19. Tong Li, Tingting Li, Houfeng Xiong, Donglei Zou. Factors Influencing Hydroquinone Degradation in Aqueous Solution Using A Modified Microelectrolysis Method. China: Water Sci Technol, 2015; 71(3): 397–404.