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Exact temperatures of Buchanan Pluggers and Chemical Changes in Bioactive Endodontic Sealers Exposed to Heat.

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Abstract:	Objectives: To evaluate the exact temperature of the Buchanan pluggers attached to Elements Free device, and to investigate the chemical changes of bioactive root canal sealers induced by heat. Materials and Methods: The Elements Free system was activated at 200 0 C. Various sizes of Buchanan pluggers were analyzed using Type-K thermocouples and a thermal camera. A resin based root canal sealer AH Plus and bioactive root canal sealers MTA Fillapex and CeraSeal were tested. The materials were characterized by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The effects of various temperatures (37 0 C, 100 0 C and 200 0 C for 1min) were investigated by X-ray diffraction analysis (XRD) and fourier transform infrared spectroscopy (FT-IR). Results: The maximum temperature was recorded on the ML plugger surface (264.73 0 C) followed by M plugger (225.541 0 C). AH Plus and CeraSeal had traces of aluminium, MTA Fillapex of sulphur, that were not disclosed in their info sheets. XRD analysis revealed a new peak formation in CeraSeal at 200 0 C. Spectral changes were evident in AH Plus. Conclusions: Elements Free system failed to attain the temperatures shown on the digital display. When it was operated at 200 0 C, the maximum temperature recorded was 264.73 0 C. All sealers tolerated heat below 100°C. AH Plus had chemical changes after heat application. Clinical Relevance: The choice of sealer should be considered when selecting the obturation technique. The more the temperature, the more the chemical alterations occurred. Practitioners should be aware of the potential chemical changes in the bioactive endodontic sealers made by excessive heat application.

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Title Page

Title: Exact temperatures of Buchanan Pluggers and Chemical Changes in Bioactive Endodontic Sealers Exposed to Heat.

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Running Title: Chemical changes in heated bioactive sealers

Keywords: CeraSeal, infrared thermography, warm vertical compaction, thermocouple, X-Ray Diffraction Analysis, Fourier Transform Infrared Analysis

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ABSTRACT

Objectives: To evaluate the exact temperature of the Buchanan pluggers attached to Elements Free device, and to investigate the chemical changes of bioactive root canal sealers induced by heat.

Materials and Methods: The Elements Free system was activated at 200^0C. Various sizes of Buchanan pluggers were analyzed using Type-K thermocouples and a thermal camera.

A resin based root canal sealer AH Plus and bioactive root canal sealers MTA Fillapex and CeraSeal were tested. The materials were characterized by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The effects of various temperatures (37^0C, 100^0C and 200^0C for 1min) were investigated by X-ray diffraction analysis (XRD) and fourier transform infrared spectroscopy (FT-IR).

Results: The maximum temperature was recorded on the ML plugger surface (264.73^0C) followed by M plugger (225.541^0C). AH Plus and CeraSeal had traces of aluminium, MTA Fillapex of sulphur, that were not disclosed in their info sheets. XRD analysis revealed a new peak formation in CeraSeal at 200^0C. Spectral changes were evident in AH Plus.

Conclusions: Elements Free system failed to attain the temperatures shown on the digital display. When it was operated at 200^0C, the maximum temperature recorded was 264.73^0C. All sealers tolerated heat below 100°C. AH Plus had chemical changes after heat application.

Clinical Relevance: The choice of sealer should be considered when selecting the obturation technique. The more the temperature, the more the chemical alterations occurred. Practitioners should be aware of the potential chemical changes in the bioactive endodontic sealers made by excessive heat application.

Keywords: CeraSeal, infrared thermography, warm vertical compaction, thermocouple, X-Ray Diffraction Analysis, Fourier Transform Infrared Analysis.

INTRODUCTION

Warm vertical obturation techniques not only produce a homogenous obturation adapted to root canal irregularities but also increase the density of gutta-percha inside the root canals [1]. The heat-induced phase transformation of gutta-percha is crucial in warm vertical obturation techniques. Gutta-percha undergoes phase transitions from beta to alpha and from alpha to amorphous with heat application [2]. The maximum temperature required to achieve the amorphous phase in gutta-percha is 60^0C [3]. Even though a low temperature is required to cause phase changes in gutta-percha, most thermoplasticized systems operate at 200^0C. Temperature rise is essential in warm vertical obturation techniques, yet, it is potentially harmful [4].

The filling ability of the warm vertical technique is affected by the penetration depth of the plugger [5] and the set temperature of the heat source [6]. To date, radicular temperatures associated with the warm vertical obturation techniques were extensively studied [7, 8]. Yet, there are limited studies on the exact temperature on the plugger surface of warm vertical obturation devices [2, 9]. The studies on plugger temperatures have been conducted mainly with System B device [8, 10]. These studies revealed that the temperature setting of the warm vertical obturation device was significantly different from the exact temperature of the pluggers.

During warm obturation techniques, gutta-percha is heated inside the canal using heat carriers. Endodontic sealers are also exposed to high temperatures when used in these techniques. Temperature rise in the root canal causes chemical changes of epoxy resin-based [4, 11] and calcium silicate based sealers [11]. A limited number of studies [4, 10-12] have investigated the effect of heat application on bioactive root canal sealers.

Therefore, the aim of our study was to investigate the chemical changes of bioactive root canal sealers induced by heat, and to evaluate the exact temperature of the buchanan pluggers attached to Elements Free warm vertical obturation device using a thermal camera and thermocouples. Our first hypothesis is that the measured temperatures on the buchanan pluggers would coincide with the settings on the digital display of the device. Our second null hypothesis is that the chemical properties of bioactive endodontic sealers would not be affected by heat application.

MATERIALS AND METHODS

Heat profiles of endodontic carriers

The heat carrier system Elements Free (Sybron Endo, EIE/Analytic Technology, USA) and new Buchanan pluggers of extra-fine (XF), fine (F), fine-medium (FM), medium (M) and medium-large (ML) sizes were used for this study. The device was fully charged according to the manufacturer's instructions before the recording sessions.

The heat generated on the surfaces of Buchanan heat pluggers was assessed using Type K thermocouples (Chromel/ Alumel) with NI9264 output module and Labview program. Thermocouples were placed in direct contact with the surface of each size of Buchanan's pluggers at 3mm increments from the tip to the 6mm length of shank. The temperature was set to 200^0C on digital display and the device was activated for 4 seconds (cut-out mode). The temperature from each point of the plugger was measured with 8 cycles of heating (4s) and cooling (60s) to get more accurate and consistent results.

Additionally, a medium size Buchanan heat plugger with 0.10 taper was set to 140^0C, 150^0C and 200^0C modes to investigate the temperature changes in these modes using both Type K thermocouples and a thermal camera (Testo 875, Testo SE &Co. KgaA, Australia). The metal probe was dyed in black ink for the thermal camera measurements. The software of the thermal camera was calibrated at 0.93 emissivity value for the black painted metal probe.

Scanning Electron Microscopy and X-ray Energy Dispersive Analysis (SEM-EDX)

A resin based root canal sealer AH Plus (Dentsply, DeTrey, Konstanz, Germany) and bioactive root canal sealers MTA Fillapex (Angelus, Londrina, Brazil) and CeraSeal (Meta Biomed, Cheongju, Korea) were tested. The compositions of materials are shown in Table 1.

Cylindrical specimens with a 4-mm diameter and 4-mm high were prepared. They were allowed to set for 48 hours at 37°C and 100% humidity in a climatic chamber. The specimens were surface-sputtered with gold and examined using Scanning Electron Microscope (SEM) (ZEISS EVO MA10, Germany). Micrographs were taken with secondary electron and back-scattered electron detectors in the SEM device.

Images at 1000X, 2000X, 5000X and 10000X magnification were captured to determine surface regularity, distribution of elements, particle shape and similarities between particles. This study used Energy Dispersive X-ray spectroscopy (EDX) for elemental analysis, characterization of materials and determination the constituents.

Chemical changes on root canal sealers after heating

The effects of various temperatures (37°C, 100°C and 200°C applied for 1 min) during warm gutta-percha techniques were investigated. The materials were mixed according to manufacturer's instructions. The specimens were subjected to 100°C and 200°C for 1 minute, then they were allowed to set for 48 hours at 37°C and 100% humidity in a climatic chamber. The sealers were then crushed to a very fine powder using an agate mortar and pestle.

X-ray diffraction analysis (XRD)

After powdering the samples, phase analysis was carried out using XRD. XRD sample holders with internal dimensions of 0.1 mm high and a 20.0 mm diameter were used. X-ray diffractometer (XRD, Bruker D2 Phaser, Karlsruhe, Germany) used Ni-filtered CuKa radiation at 30 Kv and 10 mA Cu tube with 1.54184 Å wavelength. Scans were undertaken in the range 10^0–70^0 2Θ. Phase identification was accomplished with a search-match software using the International Centre for Diffraction Data (ICDD, Pennsylvania, PA, USA. Newtown Square, PA)

Fourier transform infrared (FT-IR) spectroscopy

Fourier transform infrared (FT-IR) analysis of the sealers before and after the application of heat was performed by FT-IR spectroscopy. The samples were analyzed in the infrared spectrophotometer (JASCO FT/IR-4700) using transmitted infrared spectroscopy.

RESULTS

Heat profiles of endodontic carriers

The maximum temperature was recorded on the medium large (ML) size plugger surface of the Elements Free heat carrier system operated at 200^0C mode (264.73^0C) followed by the medium (M) size plugger (225.541^0C) (Figure 1). The rest of the pluggers did not exceed 200^0C. The peak temperatures were 115.426^0C in XF plugger, 182.861^0C in F plugger, 171.37°C in FM plugger. XF plugger showed the lowest peak temperature.

The mean temperatures were measured as 102.047 ± 5.64^0C for XF, 158.433 ± 14.156^0C for F, $164,461\pm3.672^0$C for FM, 216.733 ± 8.04^0C for M, 192.045 ± 33.752^0C for ML pluggers operated at 200^0C mode.

The highest temperature rise was observed at the instrument tip. The temperature gradually decreased from the tip to the shank (Figure 2).

The mean amount of time to reach the maximum temperature increased as the core size of the plugger increased (Table 2). It took less than 1.5 seconds for each plugger to reach its maximum temperature. Yet, there was no correlation between the core sizes and the peak temperatures of the pluggers.

The thermal profiles of the medium plugger set at 140^0C, 150^0C and 200^0C were similar. The temperatures recorded at 140^0C and 150^0C modes were almost identical.

Scanning electron microscopy and X-ray energy dispersive analysis (SEM-EDX)

SEM-EDX was used for elemental analysis, characterization of materials and determination of the constituents.

AH Plus

Scanning electron micrographs of AH Plus and corresponding X-ray energy dispersive analysis results are shown in Figure 3.

The AH Plus samples had a regular surface with uniformly distributed elements and similar particle sizes. AH Plus exhibited a large number of globular like structures.

Energy-dispersive spectroscopic analysis of AH Plus exhibited peaks for carbon (C), oxygen (O), calcium (Ca), zirconium (Zr), tungsten (W), silicon (Si). Peaks of aluminum (Al) was also present.

MTA Fillapex

Scanning electron micrographs of MTA Fillapex and corresponding X-ray energy dispersive analysis results are shown in Figure 4.

The MTA Fillapex samples had an irregular surface with uniform distribution of elements. MTA Fillapex was composed of particles of different shapes and sizes.

Energy-dispersive spectroscopic analysis of MTA Fillapex exhibited peaks for carbon (C), oxygen (O), calcium (Ca), tungsten (W) and silicon (Si). Peaks of sulphur (S) were also present.

CeraSeal

Scanning electron micrographs of CeraSeal and corresponding X-ray energy dispersive analysis results are shown in Figure 5.

The CeraSeal samples had an irregular surface with uniform distribution of elements. CeraSeal exhibited a large number of needle-like structures and different sizes of particles.

Energy-dispersive spectroscopic analysis of CeraSeal exhibited peaks for carbon (C), oxygen (O), calcium (Ca), zirconium (Zr), silicon (Si). Peaks of phosphorus (P) and aluminum (Al) were also present.

Chemical changes on root canal sealers after heating

X-ray diffraction analysis (XRD)

XRD was used in order to characterize and identify the main crystalline phases of the sealer and their changes after heating at 37^0C, 100^0C and 200^0C.

AH Plus

The X-ray diffractometry (XRD) plot for AH Plus exhibited definite peaks for calcium tungstate (ICDD: 01-072-0257) at 18.6347, 28.7436, 34.2043, 39.2300, 47.1499, 54.3474, 57.9366, 59.5277° 2θ and zirconium oxide (ICDD: 00-002-0536) at 28.0597, 31.3878° 2θ.

In Figure 6, X-ray diffractograms of AH Plus subjected to 37^0C, 100^0C and 200^0C shows main crystalline phases. Heat application did not change the crystal structure of AH Plus. There was no difference between the X-ray diffraction analysis results at different temperatures.

MTA Fillapex

The X-ray diffractometry (XRD) plot for MTA Fillapex exhibited definite peaks for tricalcium silicate (ICDD:01-073-0599) at 29.4495, 32.2603, 32.6266, 34.4064, 38.8023, 41.3468, 51.8236° 2θ, calcium silicate (ICDD:00-003-0753) at 32.1994, 32.6825, 34.2245, 41.4194° 2θ, dicalcium silicate (ICDD:01-072-1660) at 29.3779,

32.2679, 32.693, 47.4360° 2θ, silicon oxide (ICDD:00-014-0654) at 25.9773, 28.8945° 2θ and calcium tungstate (ICDD: 01-072-0257) at 18.6347, 28.7436, 34.2043, 39.2300, 47.1499, 54.3474, 57.9366, 59.5277° 2θ.

In Figure 6, X-ray diffractograms of MTA Fillapex subjected to 37^0C, 100^0C and 200^0C shows main crystalline phases. Heat application did not affect the crystalline phases of MTA Fillapex.

CeraSeal

The X-ray diffractometry (XRD) plot for CeraSeal exhibited definite peaks for tricalcium silicate (ICDD:01-073-0599) at 29.4495, 32.6266, 34.4064° 2θ, zirconium oxide (ICDD:00-005-0543) at 24.2517, 28.0597, 31.3878, 49.4255, 50.2992, 54.1759° and calcium hydroxide (ICDD: 00 002 0967) at 34.0903, 47.0864, 50.7180° 2θ.

In Figure 6, on comparing the diffractograms of CeraSeal subjected to 37^0C, 100^0C and 200^0C groups, heat application did not affect main crystalline phases, there were no detectable differences except for appeareance of the new peak in heated CeraSeal at 200^0C.

Fourier transform infrared (FT-IR) spectroscopy

In order to study the functional groups of the sealer and their interactions after heating at 37^0C, 100^0C and 200^0C, IR spectra were analyzed.

AH Plus

Infrared (IR) spectra of the heated AH Plus are shown in Figure 7. When the temperature is increased to 200^0C, two new peaks are observed at 1637 and 1554 cm^{-1} which attributed to the bending vibrations of new O-H and N-H groups formed during the epoxide-amine polymerization, respectively. On the other hand, the intensity of N-H stretching and bending vibrations attributed to the amine/diamine reagents at 3400-3500 and 1508 cm^{-1} decreased by increasing the temperature from 37^0C to 200^0C due to the high polymerization rate and consumption of starting materials at higher temperature. Similar phenomenon can be observed about the intensity of the C-O stretching vibration of ether bonds in epoxide at 1240-1245 and 1027-1033 cm^{-1}, which decreased by increasing the temperature from 37^0C to 200^0C. In addition, the intensity of Si-O-Si bending vibrations at 914 cm^{-1} decreased clearly by increasing the temperature.

MTA Fillapex

Infrared (IR) spectra of the heated MTA Fillapex are shown in Figure 8. As shown in the IR spectra of the heated MTA Fillapex, by increasing the temperature from 37^0C to 200^0C, no distinct changes are observed in the intensity and wavenumber of the bands, but an enhanced intensity is clear for the peak located at 944 cm^{-1} attributed to the Si-O asymmetric stretching vibration (v_3) of silicate.

CeraSeal

Infrared (IR) spectra of the heated CeraSeal are shown in Figure 9. IR spectra show three distinct changes at different temperature. First, the intensity of the O-H stretching vibration (3600-3700 cm^{-1}) of calcium hydroxyl ($Ca(OH)_2$) formed during the setting process increases by increasing the temperature. Second, the intensity of the C-O stretching vibrations at 1415-1417 cm^{-1} arising from $CaCO_3$ increases by increasing the temperature. It should be noted that $CaCO_3$ is formed when the $Ca(OH)_2$ molecules interact with the atmospheric CO_2 molecules [13]. Third, by increasing the temperature from 37^0C to 100^0C, the intensity of the Si-O stretching vibration of silicate at 1062 cm^{-1} decreases and then increases by increasing the temperature to 200^0C due to the formation of hydrated and dehydrated silicates at 37^0C and 200^0C, respectively.

DISCUSSION

The purpose of this study was to assess if the temperature at the tip of the Buchanan plugger was in correlation with the digital display of the Elements Free heat carrier system. The results revealed that this system failed to attain the temperatures shown on the digital display. Similar disparities were also recorded between the set temperature of System B (Kerr Dental, Amersfoort, The Netherlands) [2, 14], Touch 'n Heat (EIE/Analytic, Redmond, WA, USA) [8], SuperEndo-α^2 (B & L Biotech, Ansan, Korea), E&Q Master (Meta Biomed, Chalfont, PA, USA) [11], Friendo (DXM, Goyang, Korea), and Dia-Pen (Diadent, Cheongju, Korea) [9] systems and the real temperature at the tip of the heated plugger.

Dimopoulos *et al*. [2] revealed that the highest temperature levels were achieved at the plugger tip. It is also the main part of the plugger that comes into contact with the gutta-percha in clinical practice. We also found that the highest temperature rise was at the tip of each plugger which gradually decreased towards the shank.

At 200^0C setting, System B device achieved maximum temperatures lower than 94^0C [2] and no other statistically significant differences were found among the different pluggers used. However, at 200^0C setting, we measured 265^0C for the medium-large size plugger. The mean and the maximum temperatures of the pluggers varied among different sizes. By increasing the size of pluggers the recorded mean temperatures increased to M size and then there was a decrease on the mean value of recorded temperature for ML, while the highest peak temperature was recorded for ML. Consequently, we cannot correlate the size of the pluggers and the mean or maximum temperatures recorded. However, both M and ML pluggers exceeded 200^0C. Therefore, we would recommend the clinicians to use lower settings while operating M and ML pluggers.

The root surface temperature of canals heated with the pluggers or the temperature of warm vertical compaction pluggers has been assessed with either thermocouples [8-10, 14] or infrared thermal imaging camera [15, 16]. We used a combination of both methods as each has its own drawbacks. Thermocouples have been the traditional gold standard of temperature measurement [7]. Thermocouples measure the temperature through direct contact with one point of an object per thermocouple. Therefore, the temperature measurement is significantly affected by the closeness of the contact [9]. Poor contact of the thermocouples with the irregular root surface may possibly result in lower recordings of the outer root surface temperature measurements [7]. Multiple thermocouples can be attached to multiple points, however, temperature loss through the thermocouples is expected [9]. We placed thermocouples in direct contact with only one surface of Buchanan's pluggers at each measurement.

The accuracy of the reading of the infrared thermal imaging camera depends on the emissivity value of the material that is being analyzed [7]. The software of the material should be calibrated and then analyzed. Yet, if this constant

value is inaccurate, then the measurements would also be invalid [7]. The metal surfaces reflect the infra-red lights; therefore, the emissivity value would be very low. Because of that, the metal probe we used was dipped in black dye. The emissivity of black painted plate is considered between 0.92 and 0.94. We used 0.93 as the emissivity value.

The temperatures measured by the thermal camera were lower than those measured by the thermocouples. The thermal camera we used could capture 5 images per second. However, it only took 1.17 seconds for the medium pluggers to reach its peak temperature. The frequency of the images that the thermal camera captured might have been insufficient in measuring the precise peak temperatures. Infrared thermography is a useful method for locating areas of maximum heat production [7]. We used thermal camera to analyze the patterns of temperature change and heat distribution of the plugger.

Previous ex vivo studies have examined the root surface temperature rises during the use of warm vertical compaction devices. Floren et al [17] suggested that any heat source at or above 250^0C had the potential to cause a 10^0C temperature rise on the root surface. A significant elevation of temperature on the outer surface of the root can be potentially harmful for the periodontal ligament [14]. The maximum temperature we measured was above this critical 250^0C (264.73^0C). Unpredicted damage may occur in danger zones [18], where there is excessive removal of radicular dentin [6] or in mandibular incisors where the dentin thickness is very low [15]. Yet, we cannot directly incorporate our findings into clinical procedures. As both dentin and gutta-percha are poor heat conductors [17].

Even at the lowest temperature setting of 140^0C, the temperature of the medium size plugger ranged between 150-160^0C; which is higher than the maximum temperature required to achieve the amorphous phase in gutta-percha. Gutta-percha softens at 60^0C and melts at 100^0C with partial decomposition [19]. We recorded that the temperature of the pluggers attached to Elements Free unit varied from 99^0C to 265^0C, hence, such a breakdown is expected. Even though low temperatures are required for phase changes in gutta-percha, most thermoplasticized systems operate at 200^0C [4]. If gutta-percha burns, it leaves a residue of mainly zinc oxide, which might jeopardize a hermetic apical seal [7]. Also, several studies [4, 10, 12] showed that the root canal sealers also underwent changes after heating the sealer above 100^0C. They suggested that the temperature level should not exceed 100^0C when epoxy resin-based sealers are used with warm vertical compaction.

The mean amount of time to reach the maximum temperature increased as the core size of the plugger increased. When the activation switch of the Elements Free device is pushed, the downpack device shuts off the energy to the tip after 4 seconds, which is called the "time-out mode". Atmeh *et al.* [11] reported that all tested heat carriers reached temperature levels below 60°C when used in time-out mode, which is a safe level for most gutta-percha and sealers. "Time-out mode" can potentially prevent an additional temperature rise, as earlier studies [7, 11] suggested that a secondary heat burst produced a secondary peak of temperature rise while using heat carriers in continuous mode. However, even when we activated the Elements Free device in time-out mode, no longer than 1.5 seconds was enough for each plugger to reach its maximum temperature. Therefore, we would recommend the clinicians to operate Elements Free heat carrier device lower than 200^0C to avoid a potential risk of over-heating. Root canal sealers are classified based on their chemical structure (resin based, calcium silicate based). The knowledge of their chemical composition helps us understand their physicochemical properties and select the best material to be used in clinical conditions. Chemical composition of the sealers and changes after application of heat were determined by several techniques. Energy-dispersive X-ray spectroscopy (EDX) has been used for the elemental analysis or chemical characterization of sealers. X-ray Diffraction (XRD) is useful for identifying the main crystalline phases. Fourier transform infrared spectroscopy (FTIR) is a technique used to determine the functional chemical groups of the sealers and interpret changes induced by heat application [20, 21].

In our study, the chemical composition and element distribution of AH Plus, MTA Fillapex and Ceraseal were evaluated by EDS analysis. All tested sealers had elements that were not disclosed in their info sheets. AH Plus and CeraSeal had traces of aluminium, MTA Fillapex of sulphur. These results may be attributed to contamination during manufacture or industrial secrets. Many studies evaluated the heavy metals in MTA Fillapex and AH Plus. Our results are in accordance with previous reports [22]. Camilleri [23] pointed out that aluminum released from the dental cements can be found in the liver, plasma and brain of test animals. Furthermore, high levels of aluminum in contact with human tissues were associated with Alzheimer's disease [23].

Chemical changes of sealers were investigated after the application of heat for 1 minute. During warm filling techniques, the heat application procedure usually lasts a minute [20] The effects of various temperatures (37^0C, 100^0C and 200^0C applied for 1 min) during warm gutta percha techniques were investigated.

As the heat carrier temperature setting was significantly different from the measured temperature of the pluggers, we did not use pluggers for heat application. Oven was preferred in our study to apply a standardized temperature. The MTA Fillapex was launched in the market as a resin-based root canal sealer containing MTA and bismuth oxide as a radiopacifier. Bismuth oxide affected the hydration mechanism of MTA and its mechanical properties

[24] and also inhibited cellular proliferation [25]. This radiopacifier was associated with discoloration as a result of interacting the collagen in dentin matrix and also with sodium hypochlorite [26]. Bismuth oxide was recently replaced by calcium tungstate. The MTA Fillapex used in our study also contained calcium tungstate and XRD analysis showed the calcium tungstate phase as one of the main crystalline phases.

The information about the composition and hydration mechanism of MTA Fillapex is limited [20, 27] The XRD plot of MTA Fillapex exhibited peaks for tricalcium cilicate. It is well known that hydration of calcium silicates result in the formation of calcium hydroxide. Although MTA Fillapex contains calcium silicate, the XRD plots showed no evidence of calcium hydroxide phase formation for heated and unheated MTA Fillapex. The results observed in our study are in accordance with previous researches [20, 27]. These results might be attributed to the resinous component of MTA Fillapex. This component may affect the hydration process of MTA, required for release of calcium hydroxide.

CeraSeal has been launched recently and little information is known about it. It is composed of calcium silicates and zirconium oxide. SEM-EDS analysis of CeraSeal revealed that it also contained phosphorus element. Although no such information has been provided by the manufacturer of CeraSeal, this sealer may contain additional phosphate phase like EndoSequence by Brasseler in the USA or TotalFill by FKG in Europe. The presence of phosphate within the material provides free phosphate ions to induce biomineralization, which occurs when the calcium ions formed from hydration of the tricalcium silicate come in contact with phosphates in tissue fluids and a calcium phosphate phase forms [28]. XRD detects only crystalline structures, therefore, amorphous structures like calcium phosphate could not be identified. Further studies are needed to correlate ion release from the CeraSeal with its biomineralization capacity.

The X-ray diffractometry (XRD) plot for CeraSeal exhibited definite peaks for tricalcium silicate and zirconium oxide. CeraSeal also had diffraction peaks for portlandite (calcium hydroxide) unlike MTA Fillapex.

The chemical composition of AH Plus sealer was affected by heat application in our study. AH Plus sealer is composed of two different pastes: (I) epoxide paste and (II) amine paste [29]. When the two components are mixed, polymerization of epoxy monomer starts immediately, and curing of epoxide paste occurs by amine paste, which acts as cross-linker. The cross-linking step is dictated by the nucleophilic character of the amine and the electrophilicity of the epoxy monomer, and ring opening of the epoxy induces the formation of hydroxyl groups that catalyze the curing reaction [30, 31]. In addition, the intensity of Si-O-Si bending vibrations at 914 cm^{-1} decreased clearly by increasing the temperature. As we know, silicone oil and SiO_2 were used in the chemical composition of amine paste in this sealer. According to the Zaragoza studies [32], the epoxy matrix can interact

with SiO_2 via hydrogen bonding, decreasing the Si-O-Si bending vibrations at 914 cm^{-1}. As a result, by increasing the temperature from 37^0C to 200^0C, the reaction rate between the epoxide and amine pastes and curing evidence increases.

Several studies have reported that the heat application resulted in chemical changes in the AH Plus [11, 12, 20, 21, 33]. On the contrary, a recent study reported that AH Plus did not reveal any changes in the spectroscopic plots [34] The variations in the experimental conditions (thermo-controlled water bath) as well as the difference in the maximum temperature (97^0C) might explain the contradiction.

Camilleri [20] heated MTA Fillapex to 100^0C and reported that MTA Fillapex was suitable for warm gutta percha obturation techniques. In our study, 200^0C was also used. IR spectra revealed that the intensity of Si-O peak at 944 cm^{-1} at 200^0C is higher than that of at 37^0C. This phenomenon can be attributed to the dehydration of calcium silicates at higher temperature[35] and formation of strong coordinative Si-O bonds. An increase in the temperature resulted in dehydration of calcium silicates in MTA Fillapex. The manufacturer of MTA Fillapex indicated that the boiling point of the sealer was 150°C. They further suggested that MTA Fillapex could be used in the thermal techniques if the temperature was kept below 150^0C.

The heat did not change the chemical structure of calcium silicate based sealers [12, 20, 21, 33]. Application of heat resulted in evaporation of water from calcium silicate based sealers [12, 21]. Calcium silicate based sealers revealed changes in their chemical composition when heated, but their chemical structure were stable [11, 36].

CONCLUSION

The temperatures recorded at the tips of the Buchanan pluggers varied between sizes and were different than the temperature set on the Elements Free digital display. It took less than 1.5 seconds for each plugger to reach its maximum temperature. When the system was operated at 200^0C, the maximum temperature recorded was 264.73^0C which could be potentially harmful for the periodontal ligament. The setting of the Elements Free heat carrier device should be lower than 200^0C, especially while using medium or medium-large pluggers, to avoid a potential risk of over-heating.

The results strongly advocate the importance of identifying the actual temperature levels of endodontic heat carriers by practitioners, and the suitability of sealers to be used at the temperature achieved.

The choice of sealer should be considered when selecting the obturation technique. Practitioners should be cautious of applying excessive heat to the endodontic sealers. The use of AH Plus sealer during warm vertical compaction techniques resulted in chemical changes in the sealer. Both the tested epoxy resin and the calcium silicate-based sealers tolerated heat below 100^0C, however, higher temperature is not recommended.

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The authors deny any conflicts of interest related to this study.

Compliance with Ethical Standards

Conflict of Interest: Tulay Bakirci declares that she has no conflict of interest. Fatima Betul Basturk declares that she has no conflict of interest. Huseyin Yaltirik declares that he has no conflict of interest. Fatemeh Mohandes declares that she has no conflict of interest. Dilek Turkaydin declares that she has no conflict of interest. Mahir Gunday declares that he has no conflict of interest.

Funding: No funding was available for this study.

Ethical approval: This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent: For this type of study, formal consent is not required.

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TABLES

Table 1: The composition of materials used in this study

Root Canal Sealer	Content	Manufacturer
AH Plus	Paste A : Bisphenol-A epoxy resin, Bisphenol-F epoxy resin, Iron oxide pigments, Calcium tungstate, Zirconium oxide, Silicon oxide Paste B: Dibenzyldiamine, Aminoadamantane, Tricyclodecane-diamine, Calcium tungstate, Zirconium oxide, Silicon oxide	Dentsply, De Trey, Konstanz, Germany
MTA Fillapex	Base Paste: Salicylate Resin, Natural Resin, Calcium Tungstate, Nanoparticulated Silica, Pigments. Catalyst Paste: Diluting Resin, Mineral Trioxide Aggregate, Nanoparticulated Silica, Pigments.	Angelus Industria de Produtos Odontologicos S/A, Londrina, Brazil
CeraSeal	Calcium silicates, zirconium oxide and thickening agents	(Meta Biomed Co., Cheongju, Korea)

Table 2: Time needed for each plugger to reach its maximum temperature.

PLUGGER	TIME (S)
XF-04	0.83
F-06	1.00
FM-08	1.00
M-10	1.17
ML-12	1.50

FIGURE LEGENDS

Figure 1: The temperature at the instrument tip of a) extra-fine (04), b) fine (06), c) medium fine (08), d) medium (10), and e) Medium large (12) size Buchanan pluggers.

Figure 2: Thermal camera images (left) and heat distribution (right) of the medium size plugger at a) 1 sec, b) 3 sec, and c) 7 sec after activation.

Figure 3: Scanning electron micrographs and corresponding energy-dispersive spectroscopic analysis of AH Plus.

Figure 4: Scanning electron micrographs and corresponding energy-dispersive spectroscopic analysis of MTA Fillapex.

Figure 5: Scanning electron micrographs and corresponding energy-dispersive spectroscopic analysis of CeraSeal.

Figure 6: X-ray diffractograms of AH Plus, MTA Fillapex, CeraSeal subjected to 37^0C, 100^0C and 200^0C.

Figure 7: IR spectra of the heated AH PLUS sealer at 37^0C, 100^0C and 200^0C.

Figure 8: IR spectra of the heated MTA Fillapex sealer at 37^0C, 100^0C and 200^0C.

Figure 9: IR spectra of the heated CeraSeal sealer at 37^0C, 100^0C and 200^0C.

Figure 01

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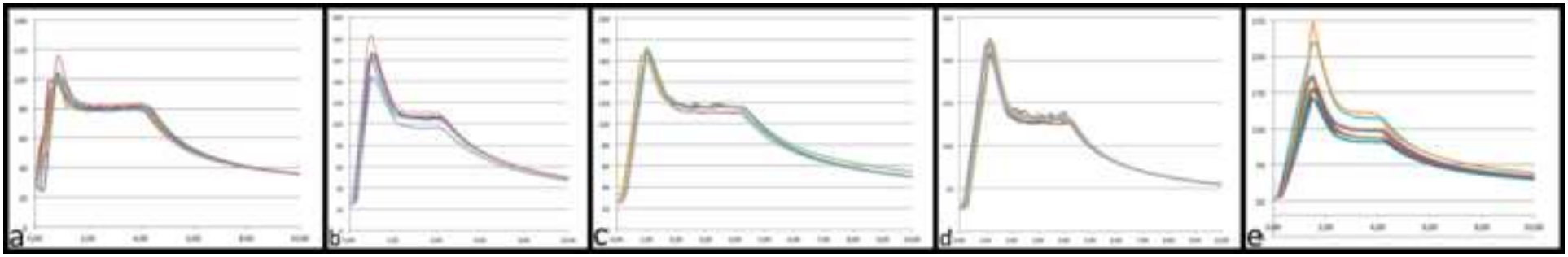

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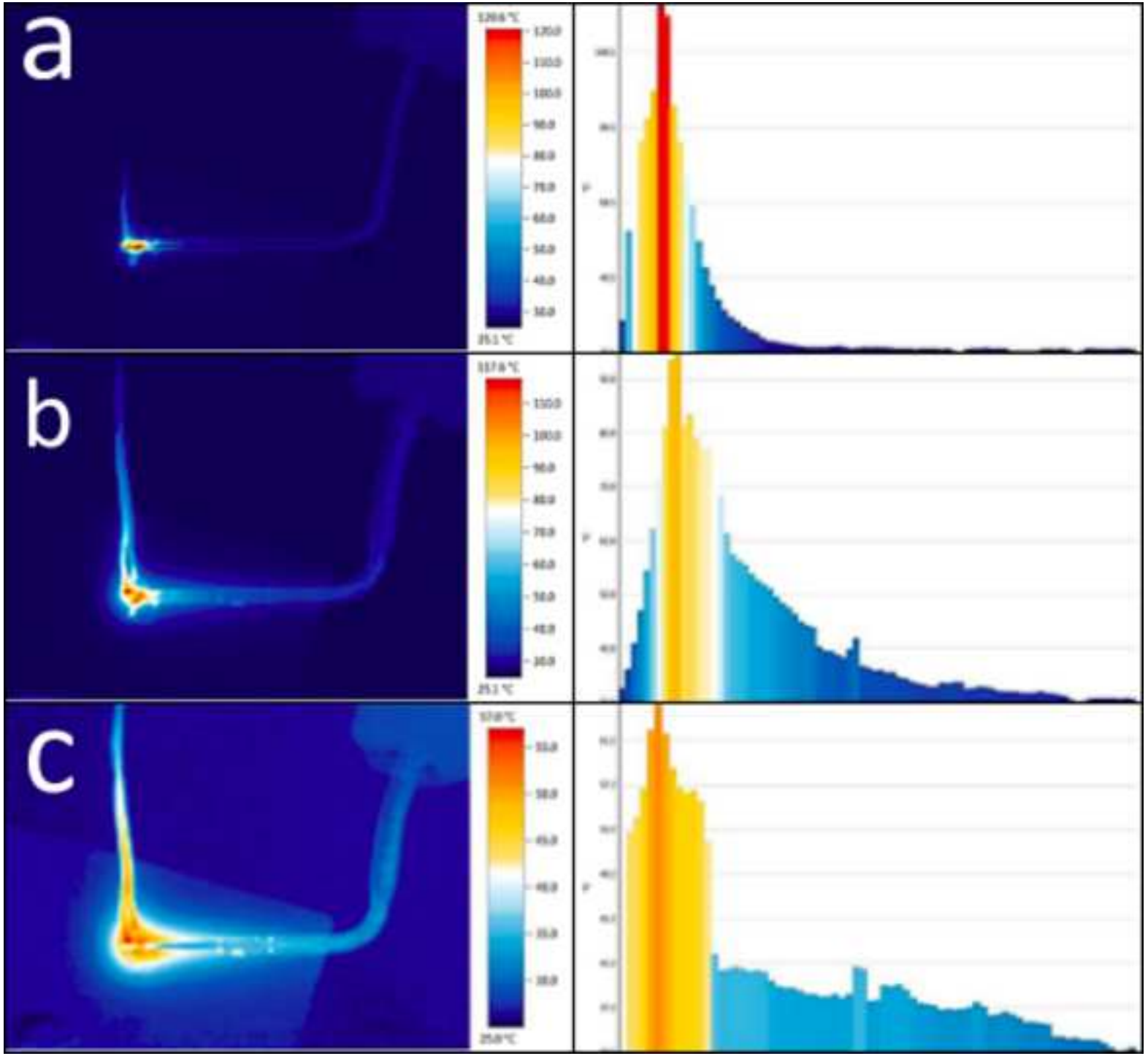

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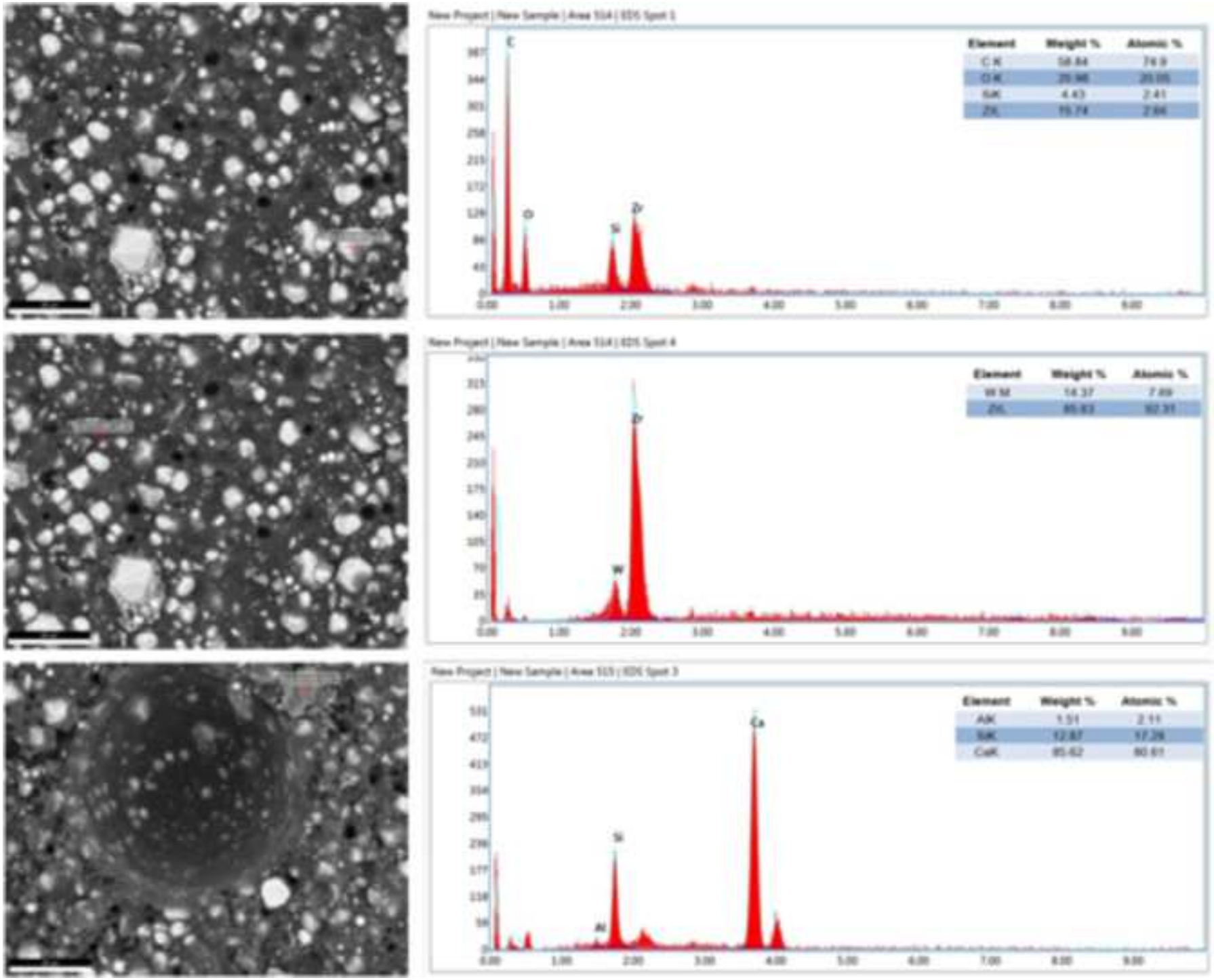

Figure 04

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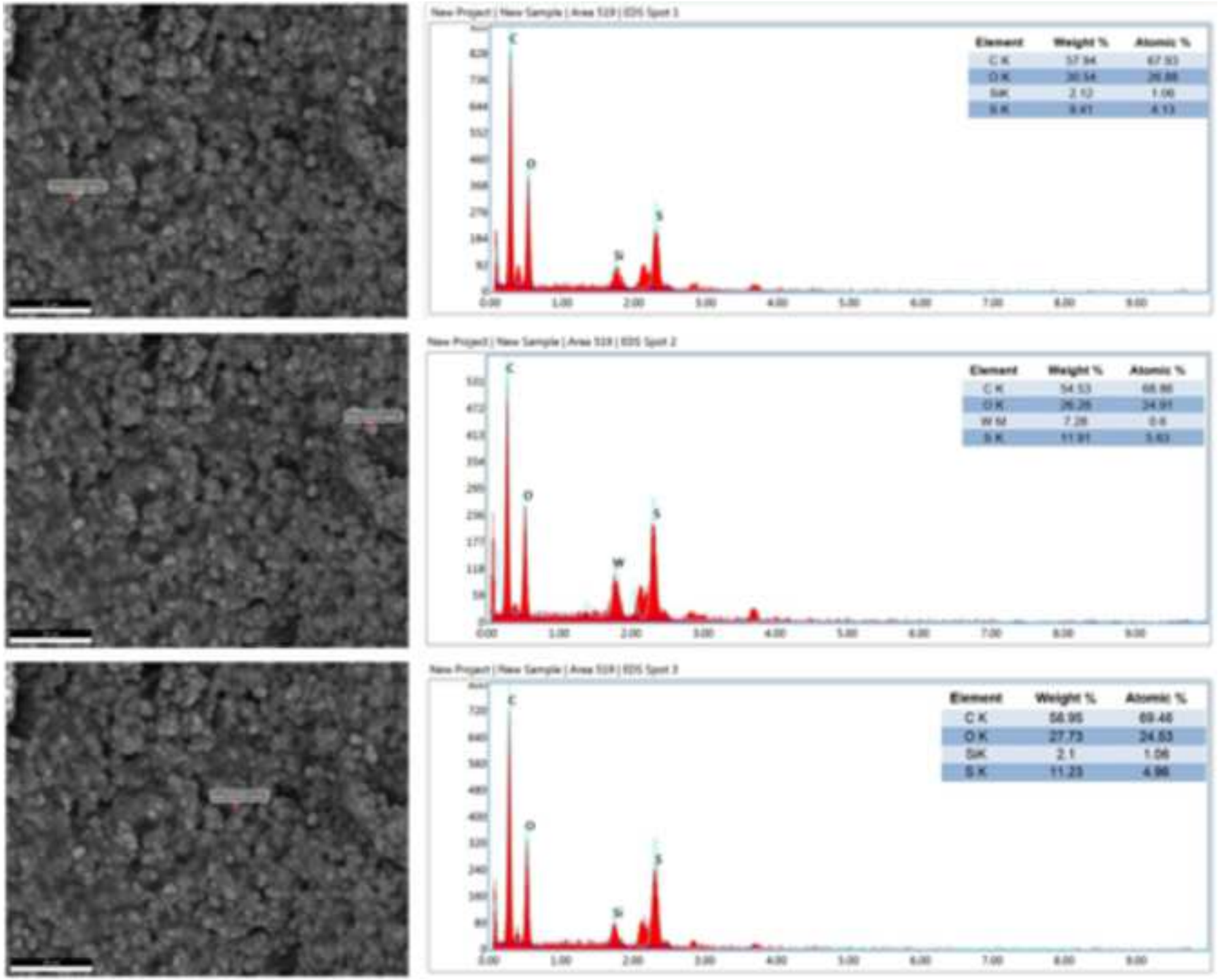

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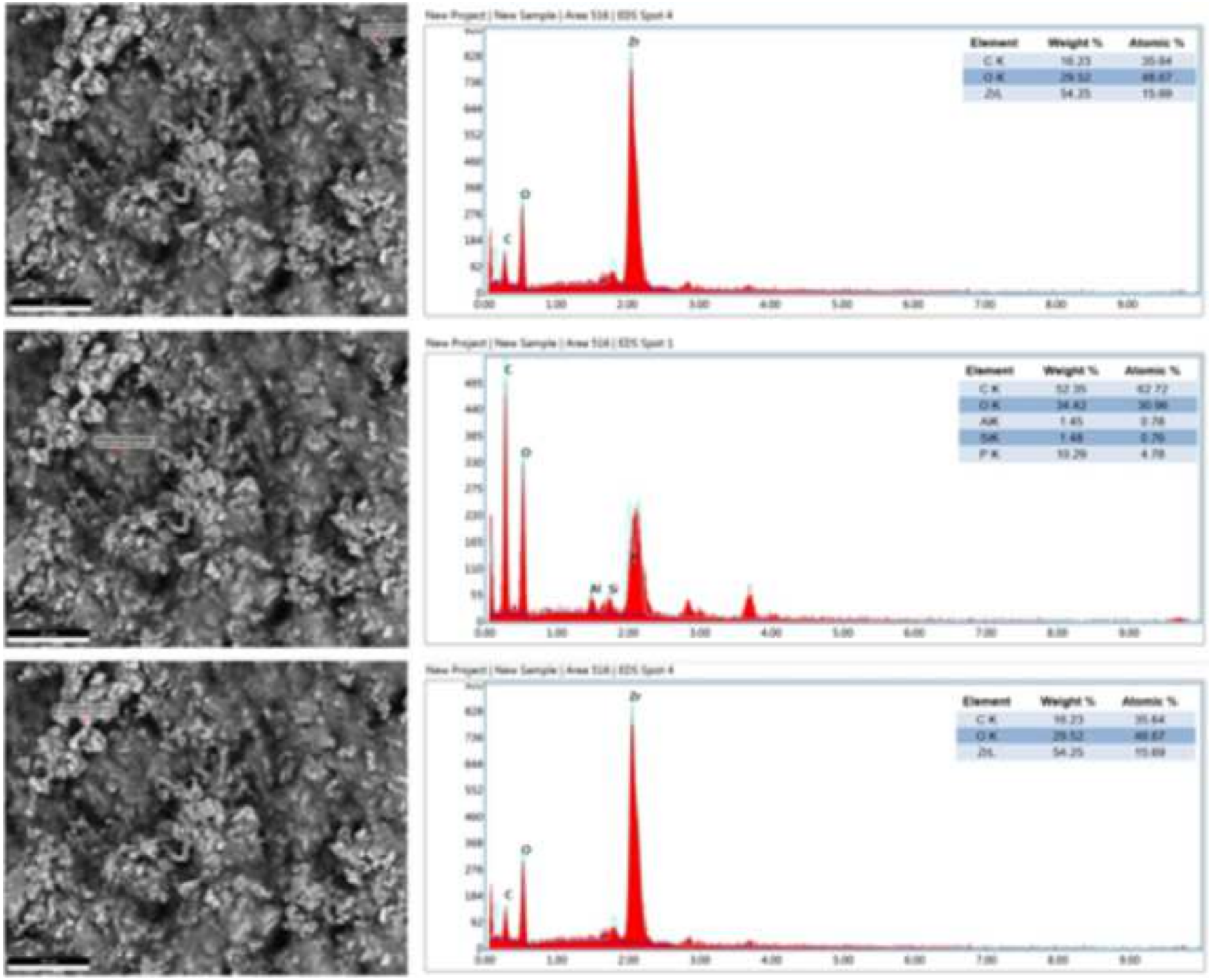

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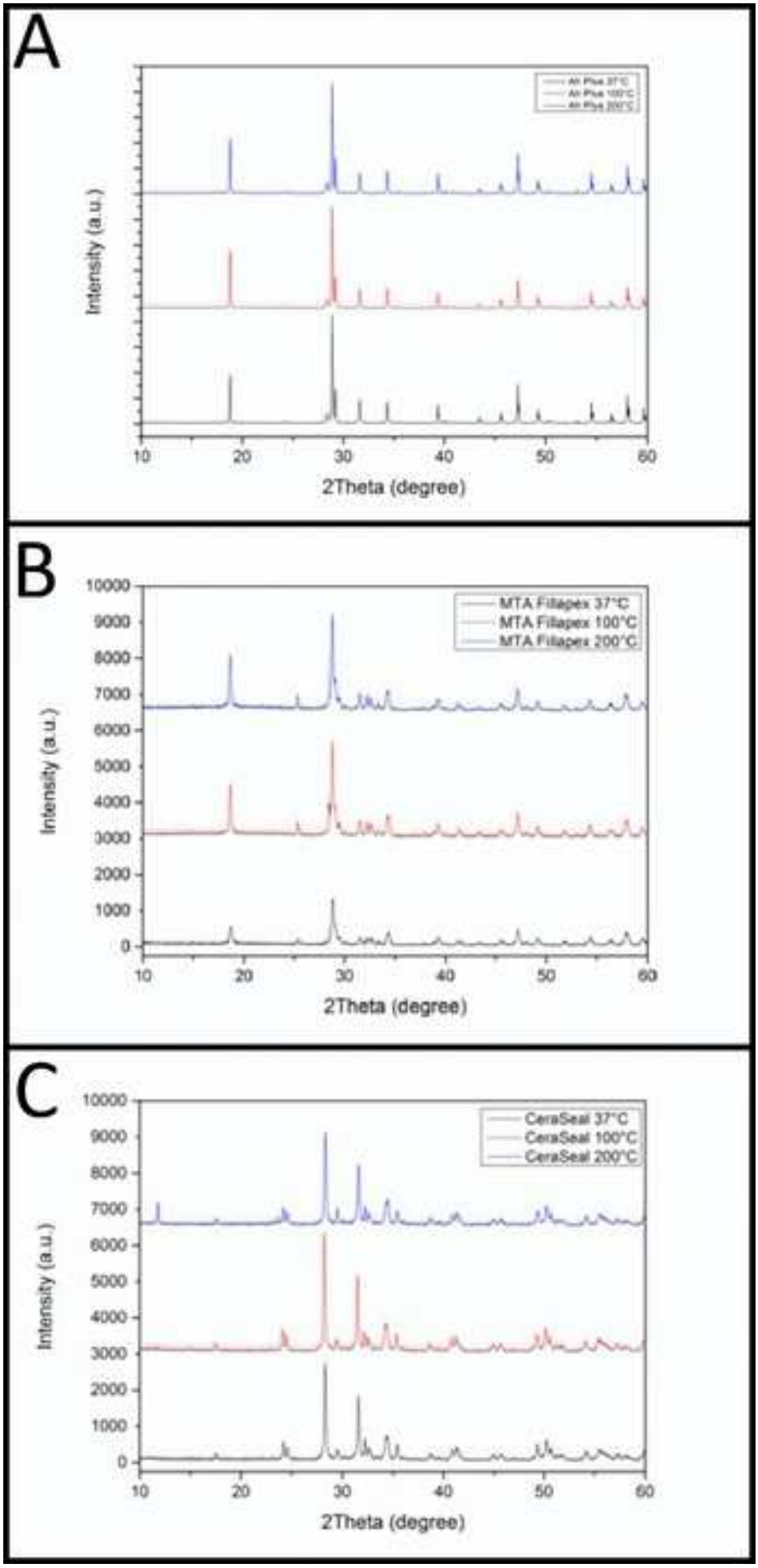

Figure 07

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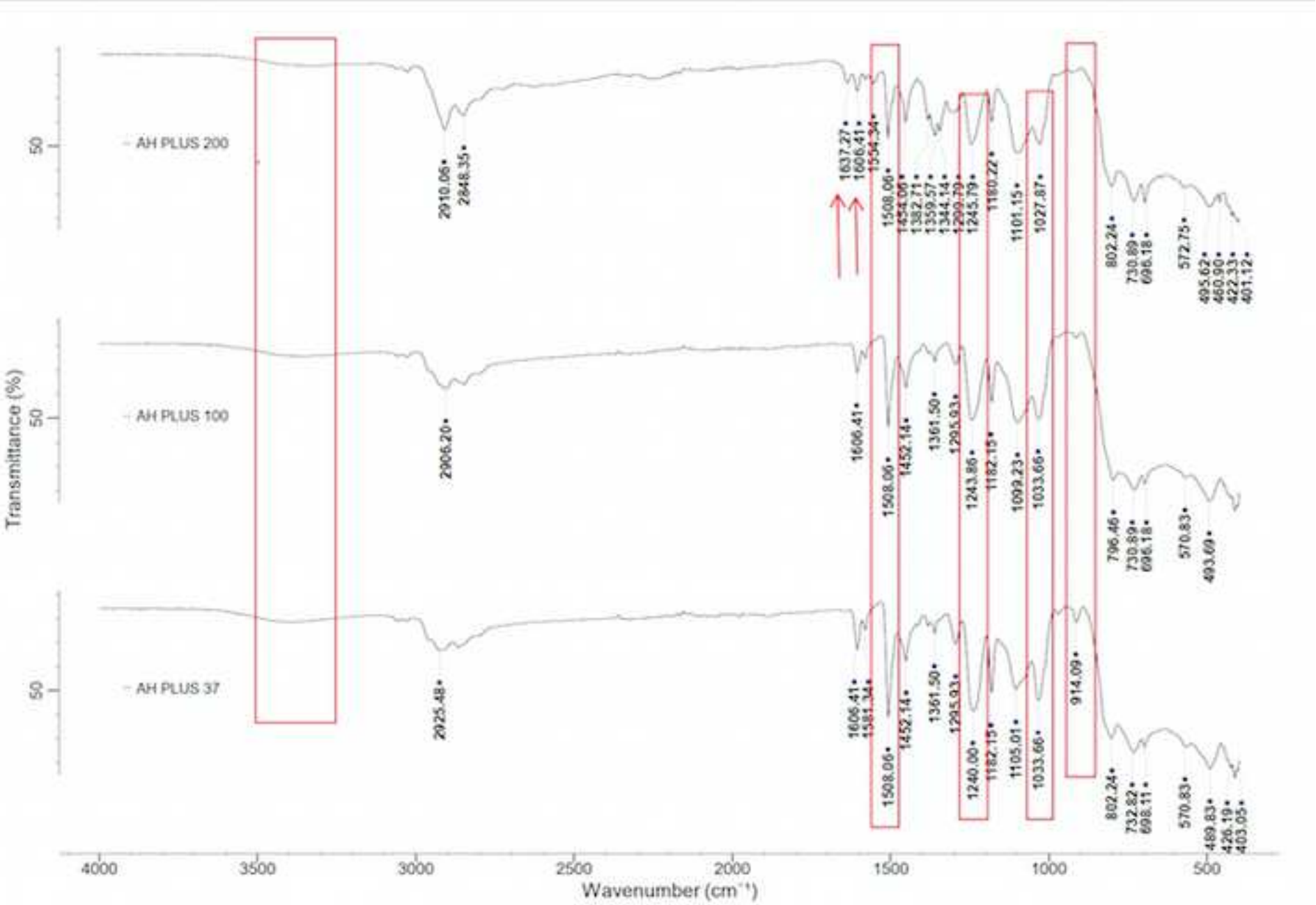

Figure 08

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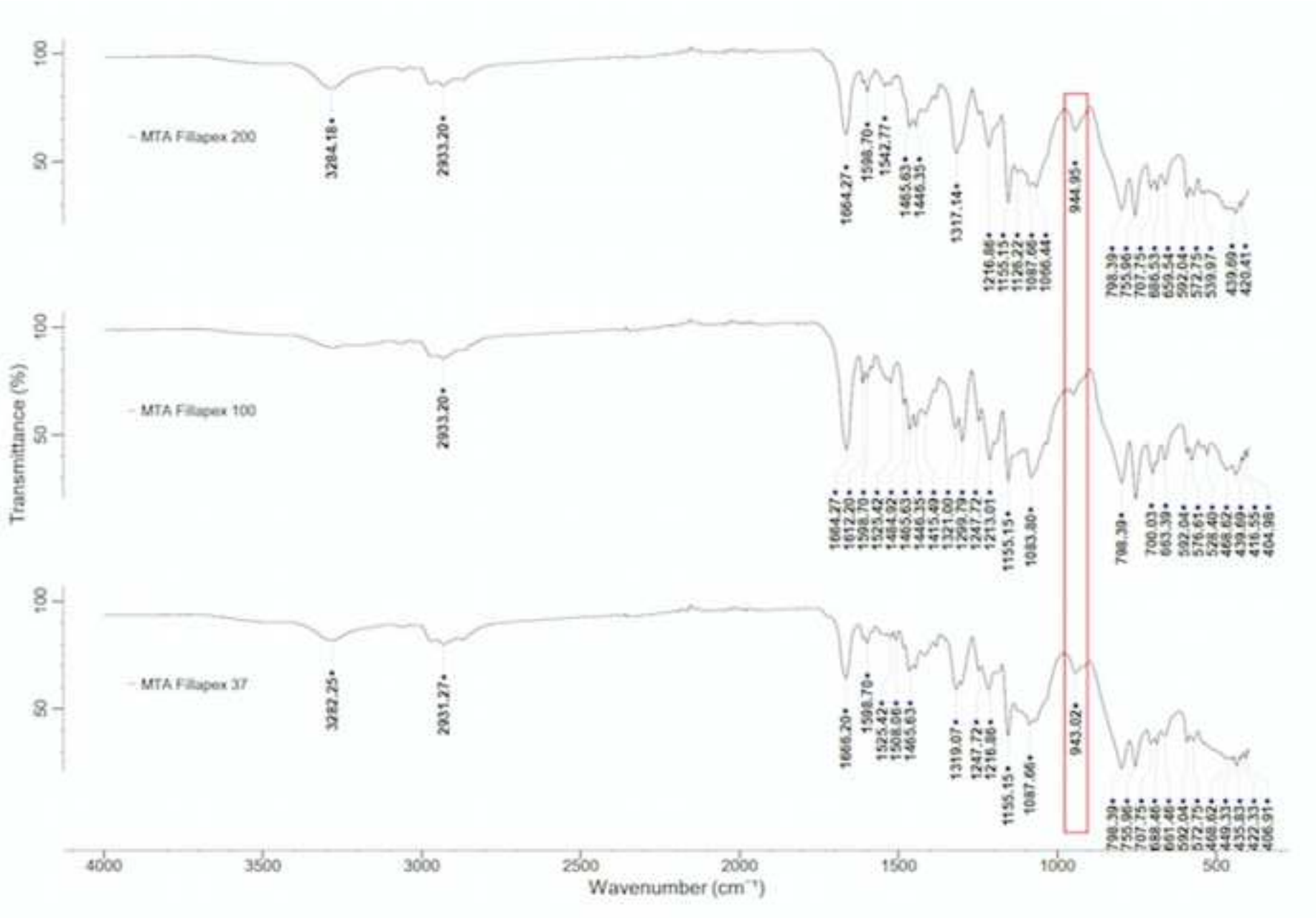

Figure 09

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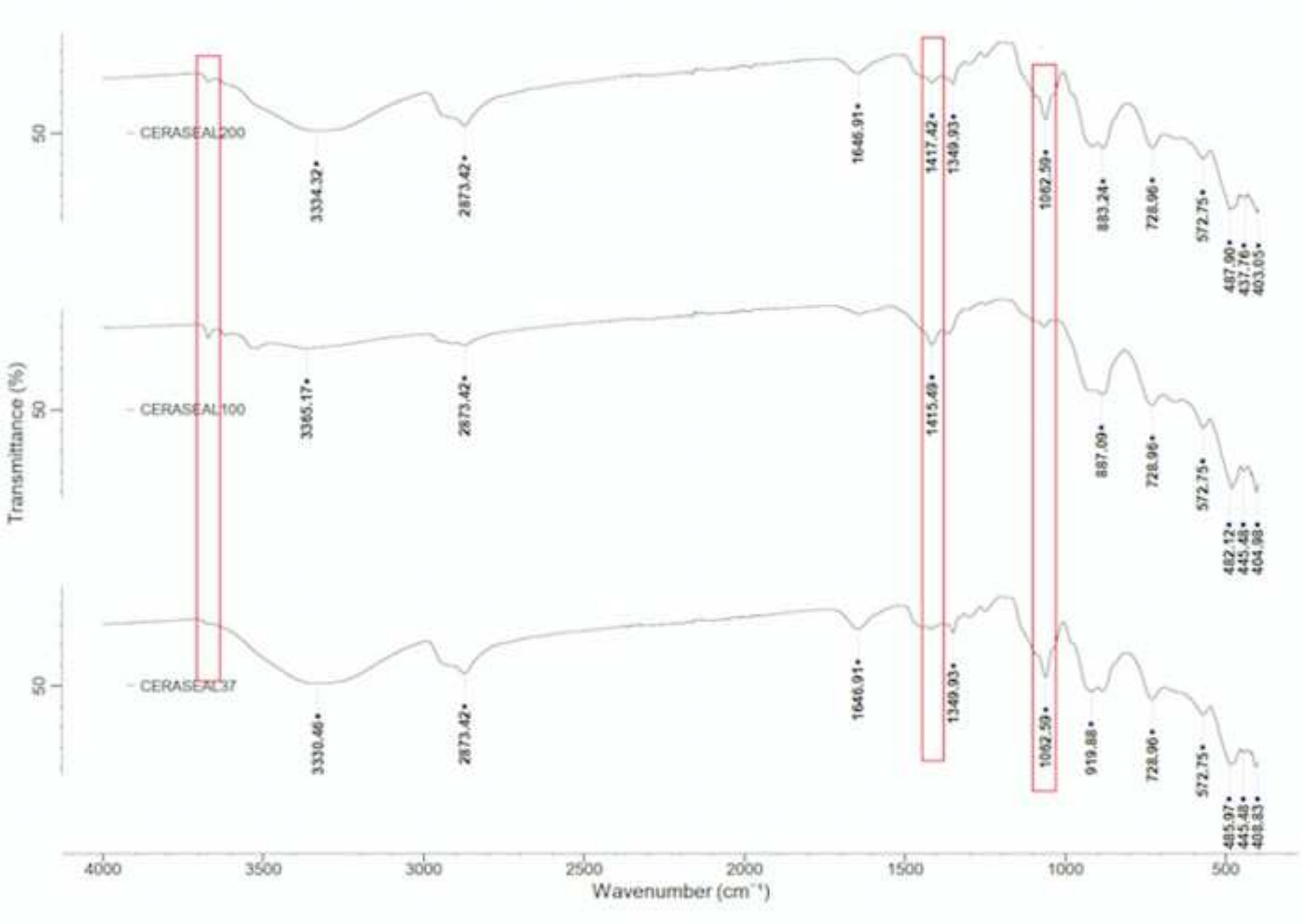

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Table 02

PLUGGER	TIME (S)
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Data Deposition Information Item