Color Coronal Spectral Analysis: Results with Water Solution of Calcium Carbonate

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Received 19/06/2023; accepted 10/12/2023

https://doi.org/10.4152/pea.2025430203

Abstract

In 2007, a study was done using color corona spectral analysis [39]. The method was applied in laboratory conditions with the coronal glow of biological objects and liquids. A high voltage of 12 kV and a frequency of 15 kHz have been applied during the research. In 1995, Antonov created the apparatus for the study, with registration in black and white photographic films. The scientist called the method selective high-frequency discharge. It has been categorized as silverless photography. In the presence of electrical conditions, electrography is at the heart of the photocopier invention. Herein, CaCO₃ in a distilled H₂O solution was tested. Comparative analysis was performed with distilled H₂O. Physical and chemical processes under high-frequency corona gas discharge conditions were analyzed. CaCO₃ was in dynamic interaction with CO₂ and H₂O at the boundary of different environments.

Keywords: CaCO₃; color coronal discharge; FTIR; H₂O.

Introduction*

Corona gas discharge produces a typical glow on devices with a 5 to 30 kV voltage and frequencies from 10 to 150 kHz [1]. In 1949, [2] received a patent for a “Method for obtaining photographic pictures of different types of objects”. The method of selective electric discharge allows for a dielectric medium to record information on another that is in contact with it. It is based on electric discharge at normal atmospheric pressure in a three-layer condenser: dielectric-air gap-dielectric [3, 4]. A constant and controllable by-force electric field is created in it. In certain places where the electric field surprises the breakdown value of the field in the air gap, a perforation in the last one occurs. Pashen’s law [5] describes this phenomenon as:

\[ V_B = f(pd) \]  \hspace{1cm} (1)

\( V_B \) depends on \( p \) and \( d \).

Due to perforation, electric discharge is selectively remitted on the recording electric medium.

In 1965, [6] has published an electrophotography book with corresponding technology for directly capturing corona discharges from biological objects,

* The abbreviations and symbols definitions lists are on pages 121-122.
especially around larger contact surfaces. Electrophotography is by far the most significant of all the reprographics technologies for photocopying and laser/LED printing.

In 1975, [7] have described the gas discharge effect with copying on the photographic photo film as electrophotography. Since 1960, [8, 9] have developed electrophotographic methods for images registration.

In 1968, [4] has developed a method for gas discharge photography. [10-18] have also made researches in this area. During the process, in the ionization zone, sliding discharge develops on a dielectric surface powered by a non-uniform electric field near an electrode with a small curvature radius. The small gap thickness between the experimental object and the electrode ranges from 10 to 100 µm.

Experimentally, the gas discharge effect gives information on the electric field distribution in the air gap between the object and the registering medium during the discharge [1, 19-21]. Ions of N, O, CO₂ and free electrons form the discharge itself. The free electrons are separated from N₂, O₂ and CO₂ molecules, which generate gas discharge between the studied object and the electrode [22-24].

Research has focused on analyzing an insight conclusion about digital analysis on the corona gas discharge spectrum, by introducing a pre-processing procedure to extract the texture effects as the radiation energy signature based on its most significant glow (digitally imaged isolines), which is used for medical biometric and disease interpretations [25].

During corona gas discharge in the atmosphere, there is a process of CO₅⁻ formation [26]. When CaCO₃, H₂O and CO₂ are combined, the following reaction is observed [27].

\[
\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 = \text{Ca(HCO}_3)_2
\]  

[28] have developed a gas discharge photography method that described the reaction as:

\[
\text{CaCO}_3 + \text{HOH} + \text{CO}_2 = \text{Ca(HCO}_3)_2
\]

Falk has shown that HOH bending is fundamental for solids and liquids [29]. CaCO₃ has the most extensive local extremums at 873 [30] and 1457 cm⁻¹ [31]. Studies employing NES and DNES [33-35] methods with 873 cm⁻¹ were made for cave water [32], the environment process [36] and plants with Ca²⁺ [36, 37]. The present investigation aimed to prove that, in coronal gas discharge conditions, there is an activation of the separated photons processes for CaCO₃ ions and H₂O reactions.

**Materials and methods**

**Device for color coronal spectral analysis**

Gas discharge emission for color coronal spectral analysis [1, 21, 23, 37, 38] was investigated in a dark room. It was registered with a photosensitive paper or color film placed on transparent Hostaphan electrode with an 87 mm diameter. It was filled with a conductive liquid composed of a 1% NaCl solution in deionized H₂O. Herein, the 1% solution was made from CaCO₃. Investigated objects (H₂O drops and human thumbs) were placed on the corresponding photosensitive
material. Pulses with 12 kV voltage and a carrier frequency of 15 kHz were applied between the objects and the electrode Cu coating. The functional scheme of gas corona discharge device is shown in Fig. 1.

![Functional scheme of gas corona discharge device.](image)

**Figure 1:** Functional scheme of gas corona discharge device.

Corona gas discharge was generated in the gap between the investigated objects and the transparent electrode, producing a characteristic glow around the contact area. Its electromagnetic emission, which ranged from 380 to 495 nm and 570 to 750±5 nm, illuminated the corresponding photosensitive material, according to the objects specific properties (Fig. 2) [39].

![Transparent electrode](image)

**Figure 2:** Transparent electrode with 87 mm diameter made of Hostaphan and filled with conductive liquid (1% CaCO$_3$ in a distilled H$_2$O solution).

Color images produced by visible, UV and IR radiation were processed and analyzed with a dedicated software package. Measured spectral characteristics were calculated in eV.
FTIR
IR-spectra of CaCO$_3$ were registered on a Brucker Vertex (“Brucker”, Germany) FTIR (spectral range: average IR- 370 ÷ 7800 cm$^{-1}$; visible- 2500 ÷ 8000 cm$^{-1}$; permission- 0.5 cm$^{-1}$; accuracy of $\tilde{\nu}$ - 0.1 cm$^{-1}$ on 2000 cm$^{-1}$) and Thermo Nicolet Avatar 360 FTIR spectrometers.

NES and DNES methods
$\theta$ was measured with a specially designed instrument, which has been described in detail by [40-43]. H$_2$O drops evaporation was performed in a sealed chamber with a stable temperature of 22 ºC and humidity from 65 to 70% [40, 43] (Fig. 3). The drops were placed on a 350 µm thick BoPET sheet.

Figure 3: Operating principle of the method for measuring the liquid drops $\theta$ on a hard surface: 1- drop, 2- thin Maylar sheet, 3- glass plate and 4- refraction ring width.

$\theta$ is a function of $a$ and $d_1$.
The device had the following technical features: monochromatic filter with $\lambda$ of 580±7 nm; H2O evaporation angle ranging from 72.3 to 0 deg; measured range of hydrogen bonds energy among H2O molecules was $\lambda$ = 8.9 ÷ 13.8 µm or $E = -0.08 ÷ -0.1387$ eV.

Luck has considered that, in H$_2$O, hydrogen bonds exist between H atom of one H$_2$O molecule and O of another [44]. Most of them are bound by the connection energy (-$E$) and the remaining are free ($E = 0$). It is accepted that $E$ has a negative value. This is known as Luck’s two-state model [45-48]. The number of hydrogen bonds between H atom of one H$_2$O molecule and O of another in a volume of H$_2$O is twice as high as the number of molecules it contains.

Part of the hydrogen bonds is restructured in the proximity of the drop surface spherical part and which produces dependence between $\delta$ and hydrogen bond energy [49-51].

$$\delta = -kT\ln[(1+\alpha)/(e^{E/kT} + \alpha)]$$  \hspace{1cm} (4)

where $k$ is Boltzmann constant, $E$ is hydrogen bond energy, $\alpha$ is the ratio of the phase space two sub-volumes related to hydrogen bonds ($\alpha = 28±8$) structuring and restructuring, and $I \ (5.03.10^{18} \ m^2)$ is H$_2$O molecules density in the hydrophobic surface layer. E and $\alpha$ values were determined by comparison with
The experiment. Expression (4) explains fraction C as \( \delta = C \gamma \) [50]. According to [43, 50], non-hydrogen bond interaction contribution amounts to 20\% of \( \gamma \) and C real value (= 4/5). Considering Helmholtz free surface energy:

\[
F = \gamma \Sigma
\]

where \( \Sigma \) is the drop surface spherical part [43]. At the instant of mechanical equilibrium, \( F \) should be minimal, i.e., \( dF = 0 = d(\gamma \Sigma) \) [43].

\[
0 = \gamma \Sigma - \gamma_0 \Sigma_0
\]

H\(_2\)O drops forced evaporation process occurs at a constant temperature of 20 °C in a hermetic camera [40]. Expressions for \( \Sigma_0 \) and \( \Sigma \) are as follows [43]:

\[
\Sigma = \pi D^2/2(1 + \cos \theta); \quad \Sigma_0 = \pi D^2/2(1 + \cos \theta_0)
\]

\[
-E/kT = C \gamma/kT
\]

\[
E = C \gamma_0(1 + \cos \theta_0)/I(1 + \cos \theta_0)
\]

During the process, \( \theta \) changes in discrete steps and characterizes hydrogen bonds average \( E \) as follows:

\[
\theta = \arccos(-1 + bE)
\]

\[
b = I(1 + \cos \theta_0)/C \gamma_0
\]

where \( b \) is a temperature-dependent parameter [52, 53]. The employed methods were NES and DNES [53-55]. They are used for research on natural waters [37, 53, 55], plants [35] and blood serum [56]. Molecular dynamics simulation was applied to investigate H\(_2\)O droplets wetting behavior on the sandstone surface under different salinities. The system equilibrium configuration was used for studying the interaction of its components. The number of hydrogen bonds was calculated [57, 58]. \( E \) of hydrogen bonds among H\(_2\)O molecules in H\(_2\)O samples is measured in eV. A non-equilibrium evaporation process of H\(_2\)O droplets characterizes \( f(E) \) of H\(_2\)O. NES is measured in eV\(^{-1}\). DNES is defined as the difference [53-55]:

\[
\Delta f(E) = f(\text{H}_2\text{O sample}) - f(\text{control sample})
\]

DNES is measured in eV\(^{-1}\), where \( f(*) \) denotes evaluated \( E \) [50-54].

**Results**

*Parameters of 1\% CaCO\(_3\) in a distilled H\(_2\)O solution obtained by color coronal spectral analysis*

Electric discharge per unit area of the recording medium can be expressed as follows [20]:

\[
\sigma = [\alpha - U_p(d_2 + \delta)/d_2] \varepsilon_0(d_2 + \delta)/\delta d_2
\]

where \( \delta = d_1/\varepsilon_1 + d_3/\varepsilon_3; \) \( T \) is electric pulse duration; \( U_p \) is VB of the air gap between experimental object and recording medium; \( d_1, d_2 \) and \( d_3 \) are the
thickness of the object, air gap, and photosensitive material, respectively; $\varepsilon_0$ (1.00057 F/m$^{-1}$), $\varepsilon_1$ and $\varepsilon_3$ are dielectric permittivity of air, experimental object and photosensitive material, respectively.

VB of the air gap is:

$$U_p = 312 + 6,2d_2$$

Consequently, a quadratic equation describing the width of the air gap is obtained:

$$6,2 d_2^2 - (\alpha T - 6,2\delta - 312)d_2 + 312 \delta = 0$$

It has the following solutions:

$$d_2 = [\alpha T - 6,2\delta - 312] \pm [(\alpha T - 6,2\delta - 312)^2 - 7738\delta)^{1/2}$$

Coronal gas discharge method has applications for researching H$_2$O drops electrical parameters in gas discharge conditions [5].

The dielectric constant as a parameter of coronal gas discharge was described by [3, 10]. It is a reliable dielectric permittivity in a homogenous medium.

The object conductivity is not practically reflected in the formation of the electric image. The image gives information on the dielectric and geometrical object characteristics, dielectric permittivity distribution and surface unevenness [5, 9].

Dielectric permittivity is determined by the ability of a material to polarize due to an applied electric field, thereby partially neutralizing it in the material. Polarization refers to the displacement or orientation of associated electrical charges under the action of a field.

Investigation with the method of color coronal spectral analysis [1, 21, 22, 37, 38] was performed on the electric glow of the control sample (distilled H$_2$O) and 1% CaCO$_3$ in a distilled H$_2$O solution (Fig. 4).

The electrode from Fig. 2 was positively charged. The negative electrode was approached until a corona breakdown voltage occurred.

**Figure 4:** Color coronal images of the control sample (distilled H$_2$O) and of the specimen with 1% CaCO$_3$ in a distilled H$_2$O solution.

Fig. 4 illustrates that the photon emission for the control sample was $E = 2.05$ eV or $\lambda = 605$ nm, and the average outcome was in the Em orange range. The result for the
1% CaCO$_3$ sample was $E = 2.98$ eV or $\lambda = 416$ nm, i.e., the average outcome was in the Em violet range. The difference was $E = 0.92$ eV. H$_2$O drop radius was 0.41 cm or $S = \pi r^2$. $S = 3.14 \times 0.41^2 = 0.528$ cm$^2$.

For the control sample, the result was $2.11$ eV/0.528 cm$^2 = 4.00$ eV/cm$^2$. The result of the 1% CaCO$_3$ sample was $2.98$ eV/0.528 cm$^2 = 5.64$ eV/cm$^2$.

The outcome of a discharge at the liquid drops point of contact with the photo film is valuable. For distilled H$_2$O, $V_B$ had 31% discharge with photons in the red Em, where $E = 1.68$ eV or $\lambda = 738$ nm. With 1% CaCO$_3$, there was 73% discharge with photons in the violet Em, where $E = 3.02$ eV or $\lambda = 410.5$ nm.

The method for brightness estimation from coronal discharge emission research was developed [19, 59].

The formula calculates $P_{\text{eff}}$ of the device for color corona discharge:

$$P_{\text{eff}} = \frac{U^2}{R} \quad (17)$$

where $U = 12$ kV. Corona discharge for H$_2$O drop was $R = 10^9$ $\Omega$. $P_{\text{eff}} = \frac{U^2}{R} = 12^2 \times 10^6/10^9 = 0.144$ W.

**Results with pH and electric conductivity**

Table 1 shows the change of parameters for 1% (w/v) CaCO$_3$ after 30 sec corona gas discharge, where $U = 12$ kV and $\nu = 15$ kHz.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Distilled H$_2$O</th>
<th>1% (v/v) CaCO$_3$</th>
<th>1% (v/v) CaCO$_3$ Gas discharge effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric conductivity (µS/cm$^{-1}$)</td>
<td>28.1 ±0.28</td>
<td>55.1 ±0.55</td>
<td>57.3 ±0.57</td>
</tr>
<tr>
<td>pH</td>
<td>7.51 ±0.75</td>
<td>9.07 ±0.09</td>
<td>9.33 ±0.09</td>
</tr>
</tbody>
</table>

There was an increase in the studied electric conductivity and pH values. The number of OH- hydroxyl groups also increased with higher pH values. There was a statistically significant difference between the 1% CaCO$_3$ solution in distilled H$_2$O before and after the coronal effect, according to the Student’s t-test at $p < 0.01$ level.

**Results of reactions with CaCO$_3$**

The research on CaCO$_3$ was performed with FTIR, which showed that the peaks at $\tilde{\nu} = 713$, 873, 1457, 1627, 1793, 2512 and 3447 cm$^{-1}$ [60, 61] (Fig. 5).

DNES of H$_2$O was studied from Temnata dupka (Dark hole) cave with Ca$^{2+}$ and HCO$_3^-$ contents of 66 and 223 mg/L$^{-1}$, respectively. A peak was observed at $E = -0.1087$ eV, $\lambda = 11.41$ µm and $\tilde{\nu} = 877$ cm$^{-1}$. FTIR analysis of CaCO$_3$ had the following results: $E = -0.1082$ eV; $\lambda = 11.46$ µm; and $\tilde{\nu} = 873$ cm$^{-1}$. H$_2$O vapor spectral range ranged from 0 to 877 cm$^{-1}$ [62]. Adsorption peaks for CaCO$_3$ were at 713 and 875 cm$^{-1}$. The results indicate that an analysis of peaks at 713 and within the interval of 873 ÷ 879 cm$^{-1}$ can be used to evaluate NES processes with CaCO$_3$ in H$_2$O and air. Since exposure to H$_2$O with different physicochemical parameters, air moisture, and thermal effects can be
assessed, the quality of CaCO$_3$ solutions and protection against CO$_2$ emissions is stronger.

![Figure 5: FTIR results for CaCO$_3$.](image)

The present study illustrates an increase in f(E) peak at 877 cm$^{-1}$, from 32.6 to 39.9 eV$^{-1}$, during the process of coronal discharge on 1% CaCO$_3$ in a distilled H$_2$O solution (Table 2).

**Table 2:** Results for 1% CaCO$_3$ in a distilled H$_2$O solution before and after coronal discharge.

<table>
<thead>
<tr>
<th>1% CaCO$_3$ in distilled H$_2$O</th>
<th>1% CaCO$_3$ in distilled H$_2$O after coronal discharge f(E) with eV$^{-1}$ of 877 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.6</td>
<td>45.3</td>
</tr>
<tr>
<td>32.3</td>
<td>44.8</td>
</tr>
<tr>
<td>32.8</td>
<td>45.1</td>
</tr>
<tr>
<td>32.8</td>
<td>45.2</td>
</tr>
<tr>
<td>32.7</td>
<td>44.8</td>
</tr>
<tr>
<td>32.2</td>
<td>44.7</td>
</tr>
<tr>
<td>32.6</td>
<td>44.9</td>
</tr>
<tr>
<td>32.7</td>
<td>44.8</td>
</tr>
<tr>
<td>32.7</td>
<td>44.6</td>
</tr>
<tr>
<td>32.8</td>
<td>45.2</td>
</tr>
<tr>
<td>average result</td>
<td>average result</td>
</tr>
<tr>
<td>32.6</td>
<td>44.9</td>
</tr>
</tbody>
</table>

There was a statistically significant difference between 1% CaCO$_3$ in the distilled H$_2$O solution after and before coronal discharge effect, according to Student’s t-test at p < 0.05 level, with r of 0.964.

**Conclusions**

Color corona spectral analysis method has been applied for studying CaCO$_3$. 
The following conclusions were drawn: a difference in the discharge parameters of H$_2$O drops was observed for 1% CaCO$_3$ in distilled H$_2$O before and after coronal discharge effect; there was an increase in electric conductivity and pH studied parameters; the number of OH- hydroxyl groups also increased with higher pH values.

During the coronal discharge process with 1% CaCO$_3$ in a distilled H$_2$O solution, this study illustrated the increase in the peak of energies distribution function for hydrogen bonds among H$_2$O molecules $f(E)$ at 877 cm$^{-1}$, from 32.6 to 44.9 eV$^{-1}$. These findings have applications for chemical processes with color corona discharge on CaCO$_3$.

There were corona gas discharge effects from the primordial atmosphere to H$_2$O. In 1952, Miller-Urey experiments were performed with gas discharge effects in laboratory conditions. Twenty organic molecules have been structured from the following inorganic compounds: H$_2$O, CH$_4$, NH$_3$, H$_2$ and electric discharge [63]. Different scientists have repeated the Miller-Urey experiment. In 1968, [64] have synthesized porphyrin using a device with U = 12 kV. In 2014, [1] investigated corona discharge and protocells synthesis with the same value [64]. In 2021, [39] published chemical reactions of polar molecules in H$_2$O with gas discharge conditions. In 2021, [65] have studied Miller-Urey experiment processes in a silica medium with U = 30 kV.

Authors’ contributions

Ignat Ignatov: conceived the research paper original idea; collected data; performed experimental work; inserted data or analysis tools; wrote the paper.

Christos Drossinakis: collected data; performed experimental work; and analyzed data obtained by experiments. Alexander I. Ignatov: collected data; performed experimental work; and wrote the references.

Abbreviations

BoPET: biaxially-oriented polyethylene terephthalate
Ca$^{2+}$: calcium ions
CaCO$_3$: calcium carbonate
Ca(HCO$_3$)$_2$: calcium hydrogen carbonate
CH$_4$: methane
CO$_2$: carbon dioxide
CO$_3^-$: carbonate ions
Cu: copper
d: gap length
DNES: differential non-equilibrium spectrum
E: energy (eV)
Em: electromagnetic spectrum
eV: electron volts
$f(E)$: energy distribution spectrum function
FTIR: Fourier transform infrared
H$_2$: hydrogen
H$_2$O: water
HCO$_3^-$: hydrogen carbonate ion
HOH: hydrogen hydroxide
LED: light emitting diode
N: nitrogen
NES: non-equilibrium energy spectrum
NH$_3$: ammonia
O: oxygen
p: gas pressure
P$_{\text{eff}}$: effective power
r: correlation coefficient
R: electric resistance
U: voltage (kV)
V$_B$: breakdown voltage

Symbols definition
α: electric pulse slope rate
Δf: frequency change
δ: surface tension
θ: wetting angle
λ: wavelength (nm)
ν: electric frequency
ṽ: wavenumber
λ: wavelength

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