2016 السنة الأولى العدد 1 Al-Kut Univ. College Journal مجلة كلية الكوت الجامعة
ISSN: 2414 - 7419

Study the Compositional Structure of Artifacts and Determine Their Ages by Used Laser Induced Breakdown Spectroscopy

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Abstract

Archaeological materials can provide important information about the timing, strength, and longevity of prehistoric trading patterns. Multi-element chemical analysis has become a common means for attributing the provenance of different kinds of artifacts (e.g. obsidian tools, pottery, and ornamental materials). Laser-induced breakdown spectroscopy (LIBS) is a relatively novel technique that is being applied to the characterization of interfaces in layered materials as an alternative to other classic surface analytical techniques. In the present work, laser induced breakdown spectroscopy has been employed to detect compositional structure of artifacts found in Iraq. An optical emission database has been designed and built through analyzing the spectrum of some pure elements via LIBS technique and compare these emission lines with database of (NIST), that been used to identifying the artifacts component and its concentration that found in Iraq land which has their geological fingerprint that represent the genetic fingerprint of these artifacts..

Keywords: Laser Induced Breakdown Spectroscopy, LIBS, Archaeological, Artifacts Ages.

دراسة البنى التركيبية للقطع الأثرية وتحديد أعمارها بإستخدام تقنية طيف الإنـهيار المحفز ليزرياً

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الخلاصة

يمكن أن المواد الأثرية توفير معلومات هامة حول قوة التوقيت ، وطولا لعمر من أنماط تجارة عصور ماقبل التاريخ. أصبح التحليل الكيميائي متعدد العناصر وسيلة شائعة لإسناد منبع أنواع مختلفة من الأعمال الفنية (مثل أدوات سبج ، والفخار، ومواد الزينة). إن تقنية طيف الإنهيار المحفز ليزرياً (LIBS) هي تقنية جديدة نسبيا حيث يتم تطبيقها على توصيف الواجهات في المواد والطبقات كبديل لتقنيات تحليلية سطحية قديمة أخرى.في العمل الحالي ، وباستخدام الليزرالذي يحفز الطيفي الإنهياري قد أستعمل لكشف الهيكل التركيبي من القطع الأثرية الموجودة في العراق. وقد تم تصميم قاعدة بيانات الانبعاثات الضوئية والتي بنيت من خلال تحليل الطيف من بعض عناصر نقية عبر تقنية LIBS ومقارنة هذه الخطوط الانبعاثية مع قاعدة بيانات (NIST)،

والتي استخدمت لتحديد عنصرالتحف وتركيزها الموجدة في أرض العراق والتي لديها بصماتها الجيولوجية حيث تمثل البصمة الجينية لهذه القطع الأثرية.

1. General Introduction

Laser induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy, in which a laser is focused on a target surface to generate plasma, which excites and ionizes the target material. The plasma emission begins on the target surface soon after the laser photon reseats the target surface. It is an analytical technique with a wide variety of applications for the qualitative and quantitative elemental studies. The analytical performance of the LIBS technique depends strongly on the choice of the experimental conditions. The main parameters which affect its performance are the laser wavelength, pulse energy, pulse duration, time interval of observations, ambient gas pressure, target properties, and the geometrical setup of the optics used [1].

The comprehensive study of archaeological or historical artifacts and works of art, that are essential components of our history and cultural heritage, often requires an in-depth knowledge of their macroscopic and microscopic structure. This can best be achieved by means of various physical and chemical analysis techniques [2].

Laser-Induced Breakdown Spectroscopy (LIBS) is a rapid elemental analysis technique, attracting the attention of the archaeologist and conservators. A typical LIBS system includes a laser, focusing optics to concentrate the laser intensity onto the sample and create plasma, collection optics coupled to a spectrometer (and detector) to collect the plasma emission and record spectra. This apparatus is generally easy to use, so operating a LIBS system doesn’t require much specialized personnel training. The main advantage in LIBS is the fact that the sampling and excitation steps can be done with only one laser pulse, making easier the analysis of the sample compared to other techniques. It is a rapid analysis technique that solid samples can be analyzed directly with little preparation before analysis, so LIBS shortens the full analysis cycle compared to most other analysis techniques and can even be used in situ. This latter ability is a distinct advantage over other comparable techniques for identifying atomic content. Indeed, in the recent literature, several examples of the use of LIBS in the analysis of pigments in easel paintings, icons, and wood polychromes have been reported, demonstrating the prospects of the technique for becoming a useful analytical tool in art and archaeology [3].

The current research project focuses on the use of LIBS in the field of artifacts to investigation their compositional structure. The chemical information was studied as a function of laser energy and irradiation regime and the number of laser shots used for the analysis. In parallel, the laser induced damages during the analysis was measured.

2. Related Work

LIBS has been applied for Archaeological since such as determine age of the artifacts. It has been used to analyze the Egyptian Islamic glaze ceramic sample from Fatimid period by analyzed of contaminated pottery to draw mapping for the elemental compositions, where LIBS used to evaluate cleaning of corroded Egyptian copper embroidery threads on archaeological textiles using laser cleaning method and two modified recipes of wet cleaning methods. This was done by following up the copper signal before and after cleaning. It was found that laser cleaning is the most effective cleaning method without any damage to both metal strips and fibrous core [4, 5]. Ahmed and Nassef [6] studied mummy's linen wrapping textile dated back to the Ptolemaic period (305 BC-30 AD). LIBS qualitative results were comparable to those of SEM-EDX results. Roberts et al. from South Africa studied the 2 million-year-old fossils and rocks in surrounding recovered from the Cradle of Mankind site at Malapa. They found that the phosphorus content is significant enough to discriminate fossil bones with relative ease from the surrounding rock which had no significant phosphorus content. The rock lines in the same spectral region were shown to be mainly from silicon, iron, and manganese. They quantify the damage to the fossils during laser removal of rock; the depth of fossil removal was measured as a function of laser fluence. The threshold fluence for maximum rock removal of depth μm was 600 Jcm^{-2}. Kasem et al. [7] used LIBS for interpretation of archeological bone samples from different ancient Egyptian dynasties. They found that buried bones are susceptible to minerals diffusion from the surrounding soil that has undergone careful analysis. Diagenesis or postmortem effects must be taken into consideration on studying dietary habits and/or toxicity levels via analysis of ancient bones.

3. LIBS Fundamentals

Laser-Induced Breakdown Spectroscopy (LIBS) also called Laser-Induced Plasma Spectroscopy (LIPS) uses a pulsed laser to generate a plasma composed of a small amount of a sample. Spectra emitted by the excited species, mostly atoms and lowly charged ions, are used to develop both qualitative and quantitative analytical information [8].

LIBS operates by focusing the laser beam onto a small area at the surface of the sample to be analyzed. When the laser pulse is fired onto the target it ablates a very small amount of material which rapidly absorbs laser energy to form a plasma plume with temperatures typically ranging from a few 1,000 to 1,000,000 K. For LIBS plasmas, the temperature is often in the range of 10,000-20,000 K. At these temperatures, the ablated material dissociates (breaks down) into excited ionic and atomic species. During this time, the plasma emits a continuum spectrum which does not contain any spectral lines and so does not provide any useful information about the individual atomic and/or molecular species present. However, within a very small timeframe the plasma will have expanded at supersonic velocities and cooled down. This entire process includes the generation and properties of the energetic laser pulse, the formation and features of the plasma and the evolution of the laser induced plasma (LIP) [9].

4. Experimental Setup

The LIBS experimental set-up is analogous to the apparatus required for traditional LIBS measurements. The basic experimental setup is the same as used in our earlier work [10]. A Q-switched Nd:YAG lasers were used that delivering about (334.7mJ) at (1064nm) having (9ns) pulse width operated at (6Hz) repetition rate. The laser beams were focused through a (10cm) quartz lens on the sample. The sample was mounted on a ground stage, which was used to provide a fresh surface after each laser pulse to avoid deep crater. The emitted radiation from the plume was collected by a fiber optics. The LIBS detection system consists of a real time spectrometers (Ocean Optics HR4000 high-resolution spectrometer) covers the wavelength region of (200-1100 nm) and its resolution (~0.02-8.4nm) FWHM. The resulting spectrum is analyzed by computer using specialized software designed. The Lab. experimental setup for LIBS analysis is shown in figure (1).

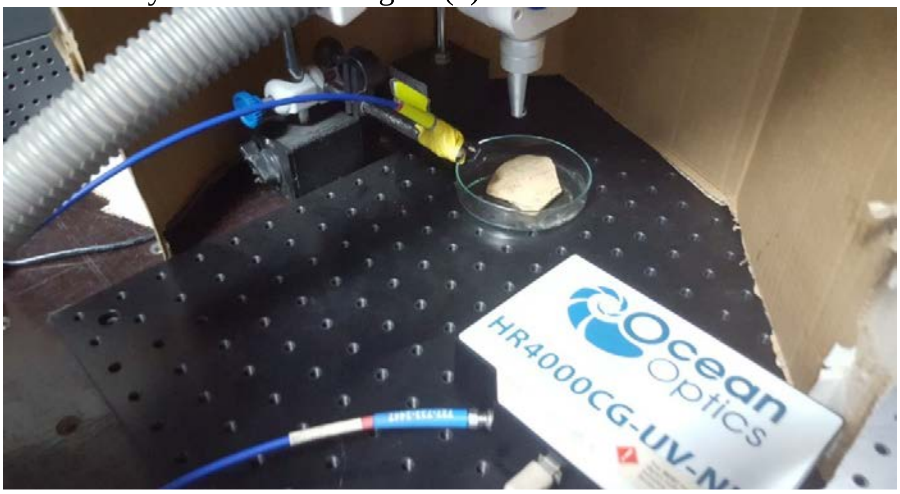

Figure 1: the experimentation procedure of LIBS system

4.1 Preparation of Samples

From our previous work “Laser-Induced Breakdown Spectroscopy (Libs): An Innovative Tool for Elemental Analysis of Soils” [10], we have been analyzed some of pure elements by LIBS technique that can be found in soil, and we have got their emission line, which represent the LIBS spectral transition of these elements. Table (1) shown the spectral transition of each elements we had tested.

Table 1: Spectral Transition of tested elements [10]

Element	Spectral Transition						
	1St	2St	3St	4St	5St	6St	7St
Carbon	391.8	426.7	514.5	588.6	657.8	-----------	-----------
Silicone	251.8	263.1	288.1	380.5	390.5	504.1	568.5
Copper	324.7	329.37	521.8	578.0	662.8	780.7	-----------
Aluminum	309.27	396.1	466.68	559.33	783.61	-----------	-----------
Gold	282.2	627.8	----------	-----------	-----------	-----------	-----------
Silver	338.0	398.1	520.9	546.54	768.77	-----------	-----------
Platinum	270.2	306.2	340.8	396.2	444.2	530.1	584.2

5. Results

We have been shot each sample of artifacts (piece of glazed pottery, piece of pottery with deeply inscriptions, piece of stained glass and piece of wood) and get its spectrum fingerprint, it has been analyzed to identified the emission line of each element by compared with NIST database as follows.

5.1 Analyses Results for Piece of Glazed Pottery

After shot the piece of glazed pottery and get its spectrum fingerprint, it has been analyzed to identify the elements and its concentration by compared with pure element reference as shown in figure (2).

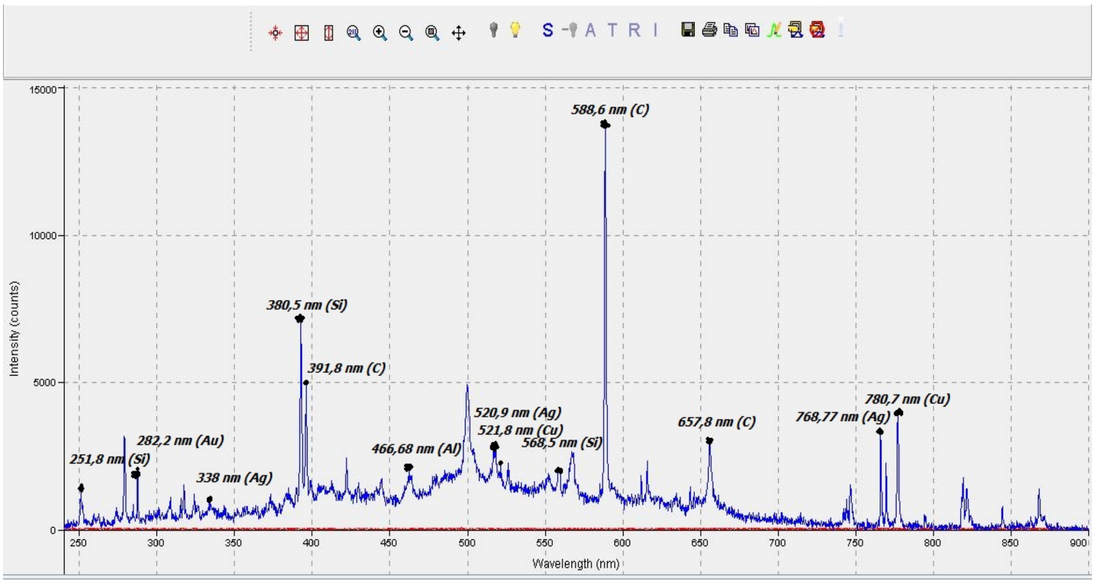

Figure 2: Emission line elements of the glazed pottery piece.

From figure (2), its shows that glazed pottery piece has thirteen identified spectrum line represent the pure elements that we tested previously. After analyzed this lane and compered with pure element it shows theglazed pottery piece has elements (Carbon, Silicone, Copper, Aluminum, Gold, and Silver) with different concentration and the tests shows there is no Platinum element in this piece. Table (2) show the spectrum lines of the glazed pottery piece and the corresponding element.

Table 2: Spectral Transition of glazed pottery piece and its corresponding elements

	Spectral Transition						
	1St	2St	3St	4St	5St	6St	7St
Spectrum line	251.8	282.2	338	380,5	391,8	466,68	520,9
Element Corresponding	Silicone	Gold	Silver	Silicone	Carbon	Aluminum	Silver
	Spectral Transition						
	8St	9St	10St	11St	12St	13St	14St
Spectrum line	521,8	568,5	588,6	657,8	768,77	780,7	
Element Corresponding	Copper	Silicone	Carbon	Carbon	Silver	Copper	

5.2 Analyses Results for Piece of Pottery with Deeply Inscriptions

After shot the piece of pottery with deeply inscriptions and get its spectrum fingerprint, it has been analyzed to identify the elements and its concentration by compared with pure element reference as shown in figure (3).

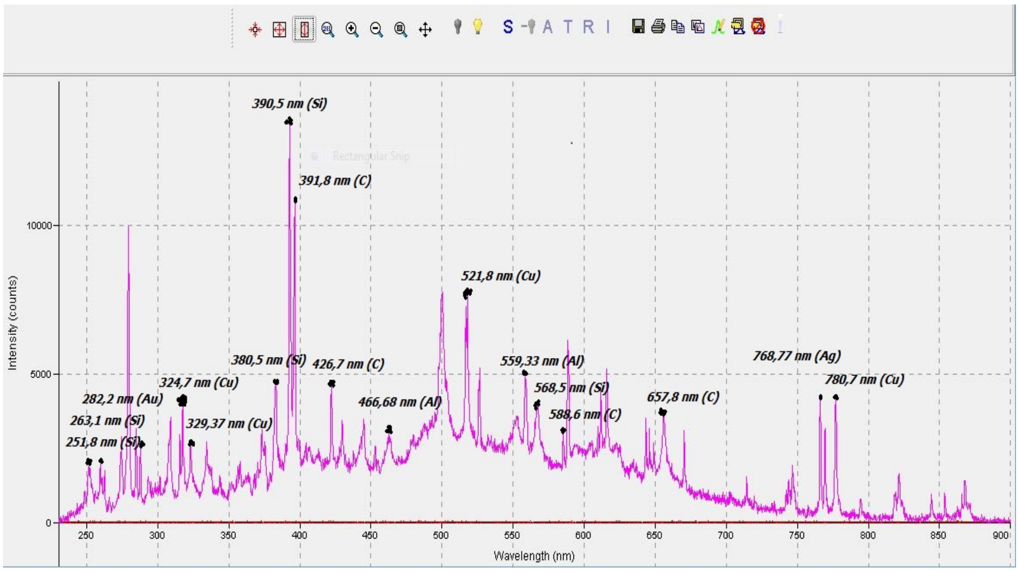

Figure 3: Emission line elements of the pottery with deeply inscriptions piece.

From figure (3), its shows that the piece of pottery with deeply inscriptions has seventeen identified spectrum line represent the pure elements that we tested previously. After analyzed this lane and compered with pure element it shows theglazed pottery piece has elements (Carbon, Silicone, Copper, Aluminum, Gold, and Silver) with different concentration and the tests shows there is no Platinum element in this piece. Table (3) show the spectrum lines of the pottery with deeply inscriptions piece and the corresponding element.

Table 3: Spectral Transition of the pottery with deeply inscriptions piece and its corresponding elements

	Spectral Transition						
	1St	2St	3St	4St	5St	6St	7St
Spectrum line	251.8	263,1	282.2	324,7	329,37	380,5	390,5
Element Corresponding	Silicone	Silicone	Gold	Copper	Copper	Silicone	Silicone
	Spectral Transition						
	8St	9St	10St	11St	12St	13St	14St
Spectrum line	391,8	426,7	466,68	521,8	559,33	568,5	588,6
Element Corresponding	Carbon	Carbon	Aluminum	Copper	Aluminum	Silicone	Carbon
	Spectral Transition						
	15St	16St	17St				
Spectrum line	657,8	768,77	780,7				
Element Corresponding	Carbon	Silver	Copper				

5.3 Analyses Results for Piece of Stained Glass

After shot the piece of stained glass and get its spectrum fingerprint, it has been analyzed to identify the elements and its concentration by compared with pure element reference as shown in figure (4).

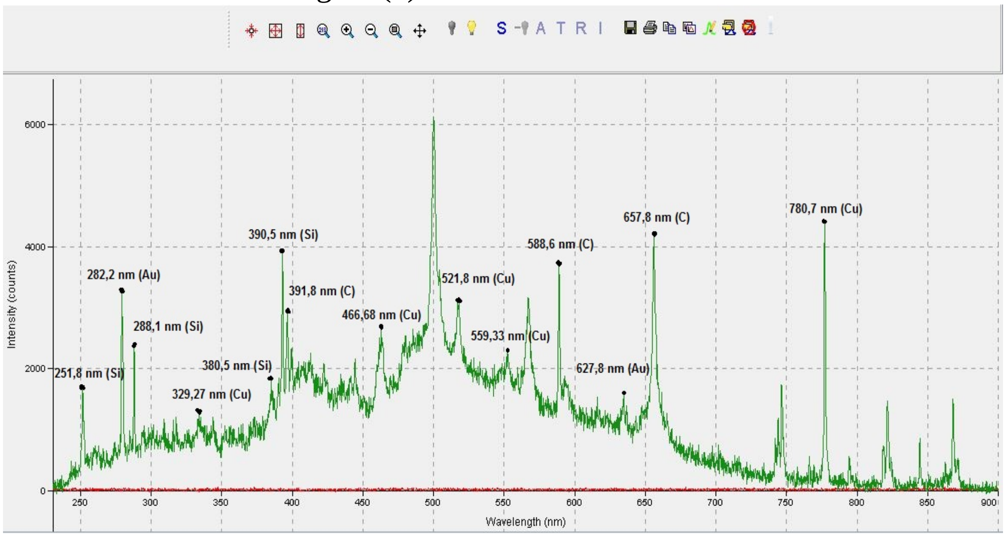

Figure 4: Emission line elements of the stained glass piece.

From figure (4), its shows that the piece of stained glass has fourteen identified spectrum line represent the pure elements that we tested previously. After analyzed this lane and compered with pure element it shows theglazed pottery piece has elements (Carbon, Silicone, Copper, Aluminum, Gold, and Silver) with different concentration and the tests shows there is no Platinum element in this piece. Table (4) show the spectrum lines of stained glass piece and the corresponding element.

Table 4: Spectral Transition of the stained glass piece and its corresponding elements

	Spectral Transition						
	1St	2St	3St	4St	5St	6St	7St
Spectrum line	251.8	282.2	288.1	329,37	380,5	390,5	391,8
Element Corresponding	Silicone	Gold	Silicone	Copper	Silicone	Silicone	Carbon
	Spectral Transition						
	8St	9St	10St	11St	12St	13St	14St
Spectrum line	466,68	521,8	559,33	588,6	627,8	657,8	780,7
Element Corresponding	Aluminu m	Copper	Aluminum	Carbon	Carbon	Carbon	Copper

5.4 Analyses Results for Piece of Wood

After shot the piece of wood and get its spectrum fingerprint, it has been analyzed to identify the elements and its concentration by compared with pure element reference as shown in figure (5).

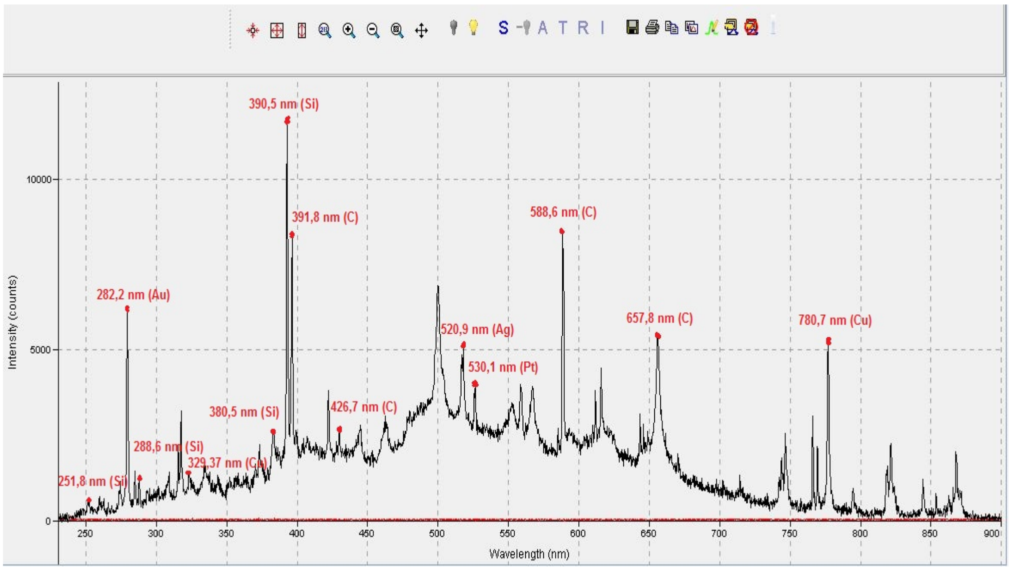

Figure 5: Emission line elements of the wood piece.

From figure (5), its shows that the piece of wood has thirteen identified spectrum line represent the pure elements that we tested previously. After analyzed this lane and compered with pure element it shows theglazed pottery piece has elements (Carbon, Silicone, Copper, Aluminum, Gold, Silver, and Platinum) with different concentration and the tests shows there is no element in this piece. Table (5) show the spectrum lines of wood piece and the corresponding element.

Table 5: Spectral Transition of the wood piece and its corresponding elements

	Spectral Transition						
	1St	2St	3St	4St	5St	6St	7St
Spectrum line	251.8	282.2	288.1	329,37	380,5	390,5	391,8
Element Corresponding	Silicone	Gold	Silicone	Copper	Silicone	Silicone	Carbon
	Spectral Transition						
	8St	9St	10St	11St	12St	13St	14St
Spectrum line	426,7	520,9	530,1	588,6	657,8	780,7	
Element Corresponding	Carbon	Silver	Platinum	Carbon	Carbon	Copper	

4. Conclusion

The emphasis of this paper was to evaluate the applicability of LIBS in the compositional analysis of archaeological pieces and determined the life span of the artifacts. From results this work shown a high ability of LIBS technique to analyze a very small amount and concentrations of the elements inside artifact sample. Thus, LIBS is very good to identifying the elements inside artifact and generate integrated spectral fingerprint for any artifact and built an integrated staid database for calibration purposes. From results, the stability of laser is an important factor that can effect on system accuracy because any increasing or reduction in laser pour density will reduce or increasing the size of generated plasma so it will effect on emitting power. Additionally the response of spectrophotometer are the main factor of detection the element concentration inside samples, so high response time side by side to are main factor to improving the LIBS system. the age calculation results of artifact shown that the LIBS system are comparable to estimated age that was determined by archaeologists of the Iraqi Public Authority for Heritage and Antiquities/public museums directorate.

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