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RESEARCH ARTICLE

Comparison of Heavy Metals Concentrations in Toothpaste Using Atomic Absorption Analysis and Laser-Induced Breakdown

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Abstract

Human health is a priority for researchers to investigate especially a toothpaste which is used daily with different types of quality. Two samples of low-quality (S1) high-quality (S2) and toothpaste were collected from the Iraqi market to be tested. This work compares two techniques, namely laser-induced breakdown spectroscopy (LIBS) and atomic absorption spectroscopy (AAS). There is a difference in sample preparation for measurement due to the two techniques. Plasma parameters such as electron temperature and electron density were calculated. Heavy metal concentrations were calculated using the calibration curve method in LIBS. After analyzing the samples, lead, zinc, mercury, nickel and cadmium were detected in the two samples, and the concentration elements were compared using the two techniques. The lead concentration was 0.3 and 0.52 in S1 and S2 toothpaste using LIBS, respectively. The concentration of mercury was 0.32 and 0.31 in S1 and S2 toothpaste using LIBS technique, respectively. Mercury appeared at a temperature of 44,800 K in sample S1 and 93,180 K in sample S2. There is a difference between the two techniques, about 15% and 10% in the first sample and 13% and 17% in the second sample for lead and mercury, respectively. These metals are dangerous to human health, so it is necessary to check these proportions due to daily use.

Keywords LIBS · Toothpaste sample · Heavy metals · Atomic absorption spectroscopy (AAS)

Introduction

Toothpaste is used by most people, either in the form of gel or powder with the toothbrush, to maintain the health and beauty of the teeth. Toothpaste is considered an abrasive that helps remove dental plaque and food residue from the teeth and helps get rid of bad breath. There are many metals used to produce toothpaste, which classify the quality of the product. However, there may be toxic metals in the components of some types of toothpaste that may cause some harmful effects on human health in general and dental health in particular [1].

A toxic heavy metal is any dense metal known for its potential toxicity, especially in terms of its presence in environmental systems. Cadmium, mercury, lead, nickel, copper, silver, chromium, and manganese are considered toxic heavy metals in the World Health Organization's List. The presence of such elements in products used daily by people represents a significant source of concern [2].

The accumulation of these elements in the human body over time causes health problems, which lead to many diseases and affect human health [3]. Therefore, it was necessary to provide a rapid-analysis technique for the chemical composition of materials. There are different analysis techniques like X-ray fluorescence spectroscopy (XRF) [4], Fourier Transform Infrared Spectroscopy (FTIR) [5], Pump-Probe Spectroscopy [6], Z-Scan technique [7] and X-ray technique [8]. The advantages of these techniques are using solid materials and do not require sample preparation in advance. The disadvantages are their applications limited due to high cost and lack of portability [9]. Atomic Absorption Spectroscopy (AAS) is a used to determine chemical

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structures by atoms absorbing light in the gas state. Calibration curves is used to detect elements and calculate concentrations, which has high analysis accuracy. The disadvantages of this technique are requiring prepare samples in advance, taking a long time of getting results, and it costs a lot comparing with other techniques, which makes it less appealing. The techniques above are expensive, not fast, and require prior preparation of the sample [10]. Therefore, there was a need for a new technique to emerge new advantages in the context of chemical spectroscopy of elements like the LIBS technique [11].

LIBS technique is a way to study elements by finding atoms or ions that come from the plasma that is made when an ablation process takes place inside a sample, which could be gaseous, solid, or liquid. The plasma energy transforms the molecules into atoms by vaporizing them, stimulating and ionizing them until they relax by emitting photons that can be detected and analyzed [12, 13]. This technique can be applied to a variety of fields and materials, such as studying the composition of soil, minerals, medicines, cosmetics, and other materials [14].

Last year, researchers gave feedback about toothpaste and LIBS techniques. In 2014, Gulab Singh Maurya et al. studied samples of toothpaste powder from different brands, and the LIBS technique was applied to detect toxic elements. Elements like calcium, magnesium, titanium, iron, and silicon were observed. Unfortunately, they did not compare the results with other techniques. The study confirmed the ability of LIBS to analyze and detect toxic elements [15]. In 2020, Liu et al. used ultrasound-assisted extraction sample pretreatment for the LIBS technique for the detection of heavy metals Pb and Cd in low-grade preparations. The results were compared using inductively coupled plasma mass. LIBS technique showed accurate results compared to other techniques [16].

The current study aimed to analyze two types of toothpaste (high and low quality) and determine the proportions of heavy metals using AAS and LIBS techniques.

Theoretical background

Estimation of electron temperature and density

One of the most essential properties of laser-induced plasma is the temperature of the electrons, which can be calculated by the Boltzmann diagram method as [17]:

$$T_e \;=\; Ek/\; K\; ln\,(\,\mathrm{I}\lambda \;/\; Ak_i g_k) \tag{1}$$

Where Ek is the highest energy level of the atom, K is the Boltzmann constant, λ the wavelength, I is the Intensity, Ak_i is the transition probability, and g_k is the statistical weight for the upper level.

The electron density is an important plasma parameter in local thermodynamic equilibrium (LTE). The electron density is calculated using [18, 19]:

$$ne \;\geq\; 1.6 \,*\, 10^{12}\, T_e^{1/2}\, ?(\Delta\, E)^3 \tag{2}$$

where ΔE is the energy difference between the lower and upper energy states in the transition lines adjacent to eV.

Quantitative determination of heavy metals in toothpaste

Concentrations are measured using the AAS technique after calibrating the device. Five standard solutions were used for each element to create a calibration curve to determine the

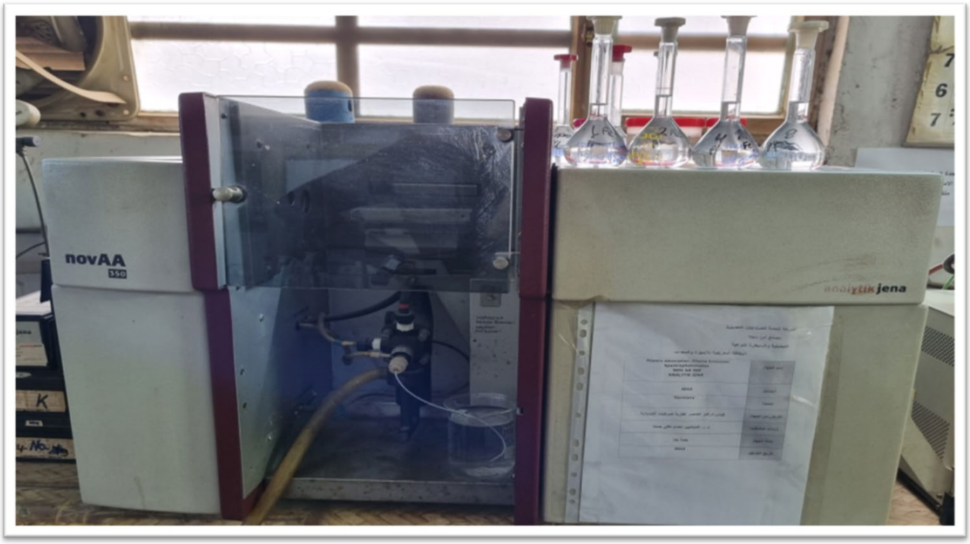

Fig. 1 The atomic absorption spectroscopy (AAS) setup in the lab

Fig. 2 LIBS setup in the lab

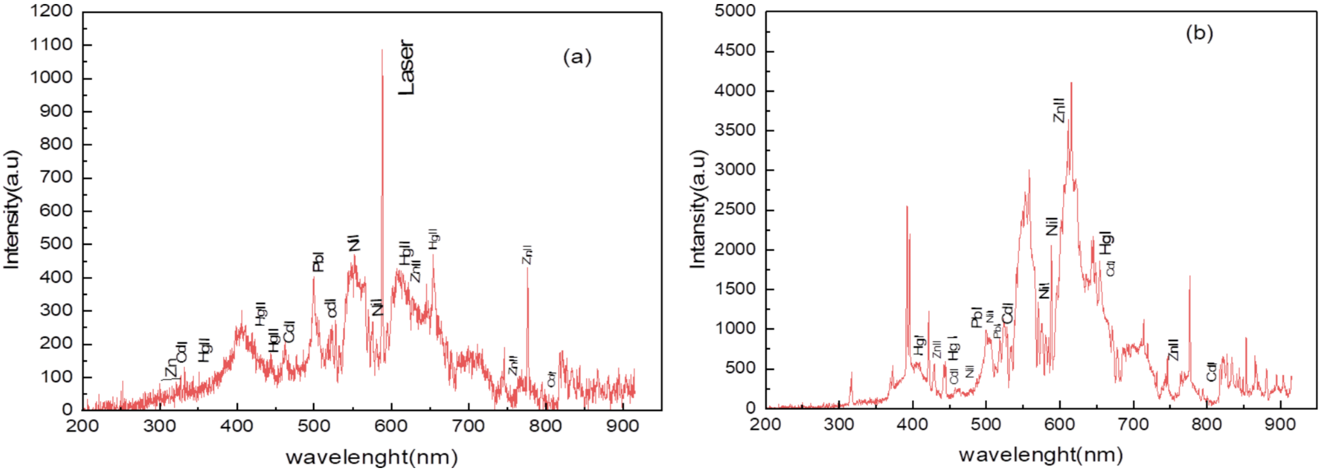

Fig. 3 LIBS spectra of Toothpaste for (**a**) sample S1 and (**b**) sample S2

concentrations of heavy metals in the samples under this study. The calibration solution is [20]:

$$C1V1 = C2V2 \tag{3}$$

Mathematical relationships were applied to estimate the element contents in the material. The electron density (n_e) was determined by analyzing the spectral lines of each element in the sample using the Eq. (2). By applying the Eq. (1), the electron temperature (T_e) was calculated. Electron density in Eq. (2) is used to determine the concentrations of elements in samples S1 and S2 as [18]:

$$Cs = \frac{\mathrm{ne}^{*}\mathrm{a}}{\sum_{i}^{n}\mathrm{ni}^{*}\mathrm{a}} \tag{4}$$

where *Cs* element concentration, n_i is ion density, *and a is the atomic number (65.39, 58.69, 207.2, 200.95, and 112.411) of elements Zn, Ni, Pb, Hg,* and Cd, respectively.

The error rate between the two techniques is calculated for each element using the relationship [21] :

$$\mathrm{R.E} = |\mathrm{x} - \mu|/\mu^{*}100\% \tag{5}$$

Where *x* is the result of AAS and *μ* is the result of LIBS.

Experimental details

Sample preparation

In this work, two types of toothpaste were randomly selected from a local Iraqi market, each with a different price range coded as S1 (low-quality brand) and S2 (high-quality brand). Actual brand names are not mentioned for ethical reasons. For the AAS technique, samples must be prepared before measurements. All glassware was washed with distilled water to avoid contamination, and then a

Table 1 Analytical data for the emission spectrum lines of the elements in samples S1, S2

Sample	Element	λ_{NIST}	λ_{LIBS}	I)a.u.)	g_kA_{Ki} (S^{-1})	Ei (eV)	Ek (eV)
S1	**Zn II**	411.939	411.99	7480	1.80E+07	12.59821	15.60713
		407.814	407.804	495	3.12E+07	12.56777	15.60713
		610.249	610.241	3110	3.73E+07	12.59821	14.62934
		758.846	758.809	159	2.20E+07	10.96481	12.598
	Ni I	464.866	464.32	253	2.20E+08	4.235705	6.302663
		480.7	480.609	217	6.60E+07	3.678477	6.257003
		558.786	558.88	3009	1.50E+06	1.935374	4.153573
		571.19	571.14	1332	1.10E+06	1.935374	4.105406
		575.468	575.83	1066	9.30E+05	1.935374	4.089279
		599.67	599.71	1597	1.60E+06	4.235705	6.302663
		405.7807	405.712	538	2.70E+08	1.320472	4.375058
		500.5416	500.509	960	8.10E+07	3.653421	6.129731
		520.1437	520.133	702	4.20E+07	3.653421	6.03641
	Pb I	401.9632	401.881	444	2.40E+07	2.660428	5.744023
		405.7807	405.712	538	2.70E+08	1.320472	4.375058
		500.5416	500.509	960	8.10E+07	3.653421	6.129731
		520.1437	520.133	702	4.20E+07	3.653421	6.03641
	Hg I	435.8335	435.794	194	1.70E+08	4.886495	7.730455
		404.6565	404.667	574	5.40E+07	4.667383	7.730455
		524.2173	524.42	1066	3.60E+05	13.08579	15.45027
		614.6409	614.964	3165	2.50E+08	11.86707	13.88269
		619.64	619.69	2734	1.20E+07	13.53804	15.53839
		652.1092	652.137	1347	3.20E+07	13.15299	15.05374
	Cd I	414.029	414.085	406	2.40E+07	5.417165	8.41089
		467.8149	467.86	206	3.90E+07	3.733659	6.3832
		533.7486	533.736	775	1.03E+09	11.12005	13.4423
		806.6903	806.645	95	2.00E+07	10.28953	11.82606

Table 1 (continued)

Sample	Element	λ_{NIST}	λ_{LIBS}	I)a.u.)	g_kA_{Ki} (S^{-1})	Ei (eV)	Ek (eV)
S2	**Zn II**	407.814	407.804	246	1.80E+07	12.56777	15.60713
		773.24886	773.249	56	1.00E+08	10.964809	12.56777
		301.914	301.948	53	4.50E+07	0	4.1054062
		308.076	308.045	43	4.40E+07	0.2123957	4.2357049
		309.712	309.741	61	1.60E+07	0.1651673	4.1672193
		311.412	311.438	34	1.70E+07	0.1090833	4.0892791
		447.048	447.043	107	1.30E+08	3.3990104	6.171632
		498.016	498.017	263	2.10E+08	3.606013	6.0948747
	Ni I	447.048	447.043	107	1.30E+08	3.3990104	6.171632
		485.541	485.576	117	2.80E+08	3.5421297	6.0949429
		498.016	498.017	263	2.10E+08	3.606013	6.0948747
		517.656	517.631	185	9.00E+07	3.8982659	6.2927068
	Pb I	357.27292	357.232	62	3.00E+08	2.66042791	6.12973122
		405.78067	405.712	228	2.70E+08	1.32047227	4.37505823
		416.80328	416.88	202	6.00E+06	2.66042791	5.63423513
		500.541642	500.509	390	8.10E+07	3.65342134	6.12973122
		520.143711	520.133	150	4.20E+07	3.65342134	6.03641049
	Hg II	317.2116	317.213	28	7.20E+05	12.7931699	16.7006053
		325.7501	325.725	77	4.00E+07	12.8786481	16.6836676
		326.4039	326.407	38	1.40E+08	13.1529893	16.9503903
		327.7846	327.771	107	1.10E+08	13.168989	16.9503903
		354.1352	354.137	73	1.20E+05	12.0383417	15.5383855
		378.9727	378.971	116	1.50E+06	15.09554	18.366193
		404.656	404.667	245	6.21E+07	4.6673829	7.7304551
		434.74945	434.741	128	4.20E+07	6.7036623	9.5547145
		438.2549	438.252	116	3.40E+05	13.0163742	15.8446203
	Cd II	325.0324	325.043	45	1.11E+07	5.47217	9.28563
		467.8149	467.86	93	3.90E+07	3.73365891	6.38319999
		806.69	806.645	21	2.00E+08	10.28953	11.826063

specific weight (0.5 g) was taken from each sample. Then, the sample is soaked in a 10% nitric acid (HCl) solution for 12 h to fragment. It was dried in an oven at a temperature of 60° for 90 min. The mixture was left uncovered overnight at room temperature. They are placed in vials designated for each model and placed in the AAS, as shown in Fig. 1. The lamp in the cap gradually heats the solution, oxidizing the elements and producing a brown color. Five standard solutions with known concentrations of the metals to be measured were prepared (Pb, Zn, Hg, Ni, and Cd). The atomic absorption spectrometer is connected to a computer to give the concentrations (ppm) of each element.

In LIBS measurement, a portion of the sample was taken and dried for an hour in a convection oven at 55°. In this technique, we do not need to prepare the sample in advance.

Experimental devices

Measurements were made using the AAS spectrometry device model 2012 (NOV AA 200), which was made in Germany. The AAS technique needs to be calibrated. Therefore, the calibration wavelength was 232 nm for Ni, 213 nm for Zi, 253 nm for Hg, 228 nm for Cd, and 283 nm for Pb. Figure (1) shows the AAS diagram used for the measurements.

LIBS setup consists of a pulsed Nd: YAG laser with a negative quality factor switch at a wavelength of 1064 nm and repetition rates of 10 Hz shown in Fig. (2). The emission spectrum from the plasma resulting from the interaction of the laser pulse with the material is collected by a connected optical fiber (SMA90S), which contains a spherical lens coated with an AR anti-reflection coating to be sent to the spectrum analyzer. A high-resolution spectroscopic analyzer

Table 2 The temperature and density values of the electrons for each sample

	Elements	T_e	n_e		Elements	T_e	n_e
S1	Zn	27,900	2.11E+18	S2	Zn	23866.84	1.04027E+18
	Ni	7900	3.35937E+18		Ni	33679.35	1.3549E+18
	Pb	9927.16	5.74611E+18		Pb	11990.56	8.3078E+17
	Hg	44,800	3.61255E+18		Hg	93180.31	8.3078E+17
	Cd	4125.61	2.03251E+17		Cd	11190.42	1.66513E+17

Table 3 The concentrations of elements in toothpaste samples using LIBS and AAS techniques

Sample	Elements	Concentration(ppm)		R.E%
		LIBS	ASS	
S1	Zn	0.066	0.069	4.34
	Ni	0.086	0.105	18.09
	Pb	0.524	0.454	15.41
	Hg	0.319	0.355	10.14
	Cd	0.0101	0.015	32.66
S2	Zn	0.0078	0.00855	8.7
	Ni	0.157	0.176	10.7
	Pb	0.34	0.3	13.33
	Hg	0.32	0.39	17.9
	Cd	0.037	0.033	12.12

(0.8–8 FWHM standard 2.1 nm) was used with an optical design (Cherney rotation) and a wide aperture (25 µm). The program used (Visual Spectra 2.1) shows the LIBS spectral lines on the computer and was compared with the National Institute of Standards and Technology (NIST) database.

Results and discussions

LIBS analysis

The scale range of the LIBS technique from 200 to 950 nm is shown in Fig. 3. The spectrum wavelength is compared with the NIST database to check metal ID. Table 1 shows the summary data of LIBS compared with NIST data, where λ_{NIST} and λ_{LIBS} are wavelengths according to the database NIST and LIBS, $AK\ gi$ is the probability of transition between level k and I, I is intensity, E_i and E_k are the energy of the lower and upper levels in eV unit, respectively. Both Excel and Origin software were used to analyze and plot the data.

After calculating the electron temperature values for each element in samples S1 and S2 using Eq. (1), one can use these values to calculate the electron density (ne) for all the elements under study using Eq. (2), as shown in Table (2).

The variation in electron temperatures observed in Table 2 can be attributed to the nature of the material, the physical and chemical properties of each element, and the way it interacts with other elements in the material. We noticed that the mercury element in S1 shows a temperature of 44,800 K, while in S2 it shows 93,180 K, and this is a difference from what we notice in the rest of the elements because of the unique properties of squeezing mercury, as it is characterized by high purity, and therefore the way it responds to the laser pulse is different.

Estimating the concentrations of elements

Table (3) shows the concentration values for each element) Zn, Ni, Pb, Hg and Cd) in the samples S1 and S2, which were calculated based on Eq. 4, and the relative error was calculated from Eq. 5.

Looking at Table (3), the two elements Pb and Hg have the highest concentrations in the AAS technique with (0.454 and 0.355) and in the LIBS technique, the concentration values (0.524 and 0.319) in sample S1, while the concentrations (0.3 and 0.39) and (0.34 and 0.32) for sample S2, respectively. These leaks are within the permissible limits, according to the Environment Agency and other regulatory authorities. These elements are considered toxic even at low levels of presence, as their accumulation in the body over time causes various health problems, such as their effect on the digestive system, growth disorders, kidney problems, soft tissue disorders, and cancer of various types [22, 23].

Looking at Fig. 4, the measured elements (Ni, Pb, Hg, Zn, and Cd) according to AAS and LIBS techniques show similarity in estimating the calculated concentrations to some extent. The small amount of difference results from the mismatch of the spectral lines in the LIBS technique because of the Stark Broadening. This is caused by the broadening of the spectral lines that is proportional to the density of electrons in the plasma. The higher electronic density leads to higher Stark Broadening [23]. In the AAS technique, it may be the result of a chemical reaction between the components of the sample and the solvent or the surrounding environment, which can cause changes in the absorption of light that lead to inaccuracy in the measurement [24].

Zinc (Zn) and cadmium (Cd) show a good match compared to other elements in error rate R.E results. There is a difference in R.E data which lead us to think a need to improve analysis methods, such as device calibration or sample preparation methods.

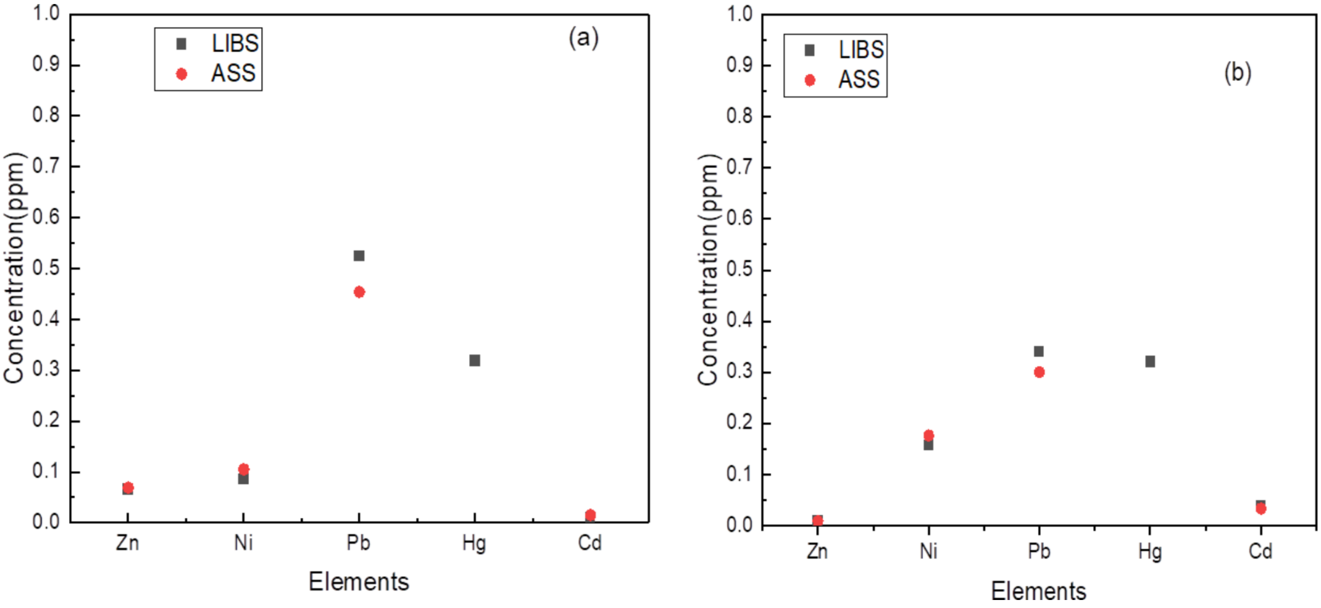

Fig. 4 The concentration metals detected by LIBS and AAS technique for (**a**) sample S1 and (**b**) sample S2

Conclusion

In this work, two main techniques are used to analyze metals in toothpaste, namely AAS and LIBS. The results showed that LIBS is an effective and low-cost method for extracting metal concentrations in toothpaste compared to AAS. The concentrations of lead and mercury were the highest values in both samples, exceeding the permissible limit of the Environmental Protection Agency. For daily use, these elements are toxic elements and their accumulation in the human body as a result of daily use causes harm to the human body.

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