Proc. 2nd Saudi Sci. Conf. Fac. Sci., KAU, 15-17 March 2004, **Part II,** pp. 139-146 (2005 A.D./1425 A.H.)

Compositional Study of Different Currency Coins Using Non-Destructive Laser Induced Breakdown Spectroscopy

ZAIN H. YAMANI

Department of Physics, King Fahd University of Petroleum & Minerals, Dhahran, Saudi-Arabia

e-mail: zhyamani@kfupm.edu.sa

ABSTRACT. Laser induced breakdown spectroscopy (LIBS) is implemented to study the compositional content for coins of different currencies. Laser-induced plasma fluorescence spectra in two regions of the visible spectrum show qualitative similarities in the compositional content among Saudi, Bahrain and Euro coins. However, a game-token shows some of distinction.

The sample exposure to laser radiation lasts for a few seconds and the laser analysis is dependable and non-destructive. Hence, LIBS can be beneficial for the identification of currency and also for quality control in coins production.

Introduction

There is a growing interest in the development of detection systems for rapid and accurate analytical characterization of chemical species present in rocks, minerals, waste disposal sites, soil and water samples. Modern instrumental techniques are now replacing the conventional, time-consuming and laborious techniques of wet-chemieal analysis.

Innovative laser based techniques are being developed for real time analysis of samples. In particular, laser-induced breakdown spectroscopy (LIBS) is a useful method for determining the elemental composition of various solids, liquids and gases. In this method, a focused laser pulse serves to vaporize, atomize and excite the sample material. The resulting emission from the created plasma is collected by a lens and/ or optical fiber and is analyzed with an optical multichannel analyzer or with a scanning monochromator in conjunction with a photomultiplier. The atomic spectral lines can be used to determine the elemental composition, or to register the fluorescence 'finger-print' of the sample.

LIBS technique is useful for a variety of applications. It is used in environmental monitoring to measure soil contamination (Zolotovitskaya *et al.*, 1997) and to detect toxic metals (Yamamoto *et al.*, 1996; Buckley *et al.*, 2000) in the environment (Carranza, 2001; Tran *et al.*, 2001). Also, it is used to study the chemical compositions in liquids (Yueh *et al.*, 2002; Samek *et al.*, 2000) and polymers (Sattmann *et al.*, 1998). LIBS is also used in forensics and military applications (Kincade, 2003), and in biomedical studies of bones and teeth. In addition it is used for art restoration (or conservation), by analyzing pigments and/or precious and ancient metals (Anzano *et al.*, 2002).

There are many advantages for chemical analysis using LIBS. Very little, if any at all, sample preparation is needed. The same system can analyze gas, liquid and/ or solid samples with minor adjustments (Fichet, *et al.*, 2003). Moreover, LIBS samples only very small amounts of the material under study, typically in micrograms; so, it is practically non-destructive (Weritz *et al.*, 2003). Moreover, selected local analysis can be performed with a spatial resolving power of microns. A book that discusses many aspects of LIBS is that by Lee (Lee, 2000).

In the current experiment, the third harmonic of a Nd-YAG produces UV pulsed laser radiation. The laser beam is focused onto coins of Saudi, Euro, and Bahrain currency, in addition to a token used for games. The fluorescence from the generated plasma is collected and the atomic emission lines are spectrally dispersed using a grating monochromator and detected with a photodiode array (PDA) over an approximately 440 Å range.

LIBS spectra are recorded in two regions of the visible spectrum. The analysis shows that the LIBS system can identify the basic elemental composition of the four coins. The spectra can be used to identify, and distinguish between, the currency coins, on the one hand, and the game token, on the other hand. Moreover, it is verified that the 20 cent Euro currency is free of nickel.

Experimental Method

Figure 1 shows a schematic of the experimental setup. The third harmonic of a Nd-YAG [Spectra Physics, Model GCR 250] emits 355 nm laser radiation at a repetition rate of 10 Hz, and the pulse duration is ~8 nsec.

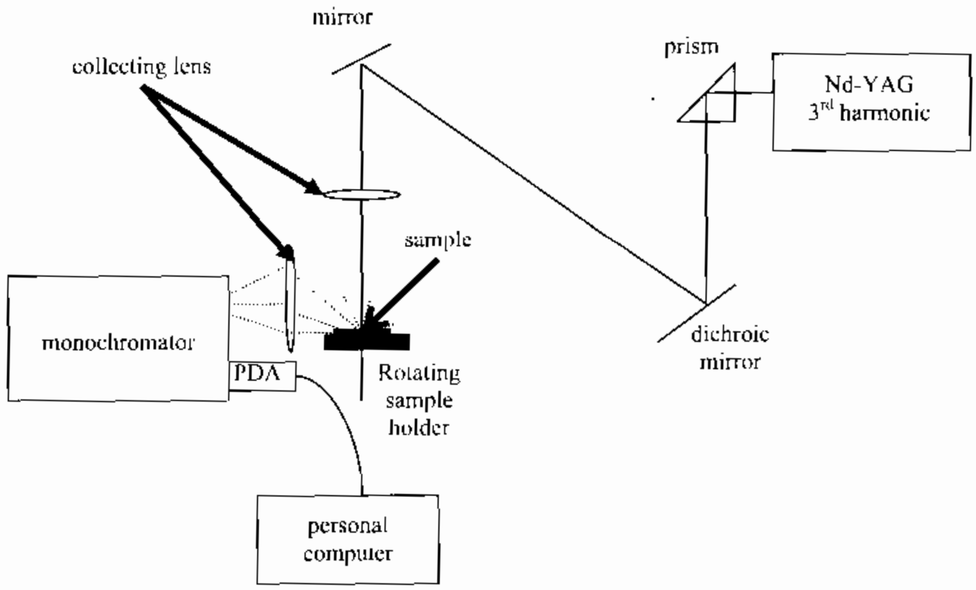

Fig. 1: Schematic plan of the experimental setup.

The laser beam is focused on the sample under study which creates fluorescing plasma. A 5-cm converging lens collects the laser-induced plasma fluorescence onto a monochromator [500 M Spex]. A Jobin Yvon ISA Photo-detector Array (PDA) [model: spectraview-1D] detects the dispersed fluorescence with its 1024 array of diodes. The Spectra Max software controls the monochromator grating motor and collects data that is stored on a personal computer for further analysis.

Deliberately, low laser power (~2 mJ per pulse) was used and the sample was mounted on a rotating sample holder in order to reduce the damage suffered by the sample. The integration time was 30 seconds. This, however, was sometimes found to he too long and occasionally caused saturation of the PDA.

Two regions were studied: 4000-4440 Å, and 5250-5550 Å. The PDA was calibrated against well-known Hg lines emitted by the room fluorescent bulbs. Fe lines from iron pellets were also made use of.

Results & Discussion

Figure 2 shows the LIBS spectra of a 10 mole % iron pellet prepared in a KBr matrix, iu the region 4000-4440 Å. The figure shows the results before the PDA was calihrated. The main peaks are indicated on the plot.

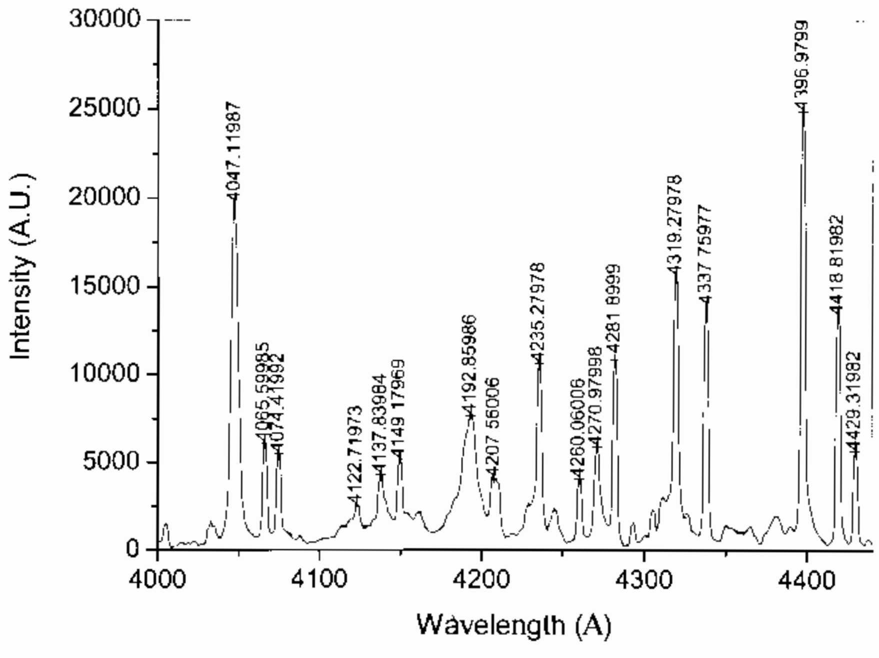

Fig. 2. LIBS result for 10% iron in a KBr matrix.

The NIST web-page (http://physics.nist.gov/cgi-hin/AtData/lines_form) was taken as reference to determine the strong Fe peaks iu this region; this includes: 4045.8, 4063.6, 4071.7, 4271.8, 4282.4, 4307.9, 4325.8, 4383.5, 4404.8 Å. Using these strong Fe peaks, in addition to the Hg peaks at 4046.6 Å and 4358.3 Å, the PDA was calibrated in wavelength for this region. A similar calibration was made in the 5000 Å region.

Figure 3 shows the LIBS result for a 25 Fils Bahrain coin, in the 4000-4425 Å region. The front and back sides were analyzed and the spectra are basically identical. This is a natural result assuming uniformity in the chemical composition of the coin. The same result applies to other coins that were studied. This indicates that LIBS technique has a high level of repeatability.

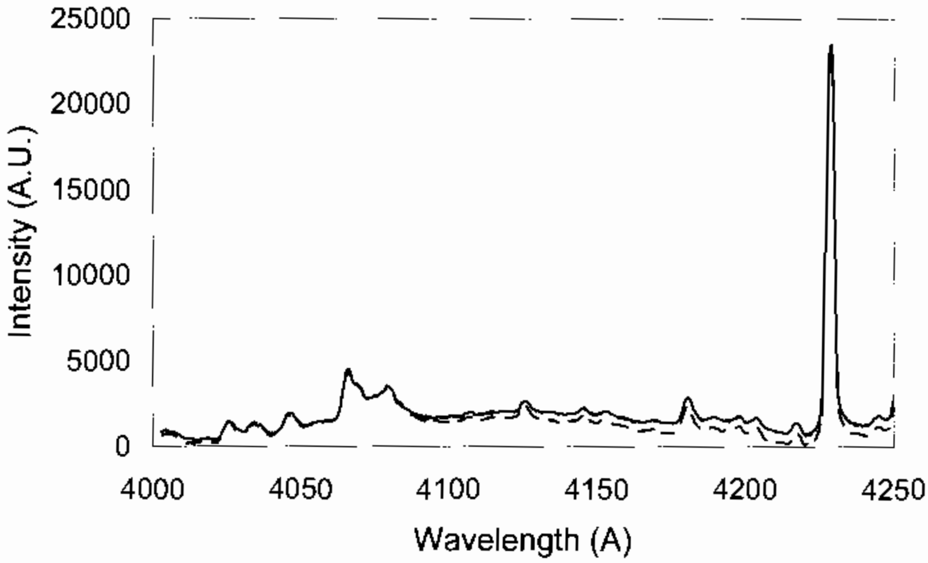

Fig. 3. LIBS spectra for (solid) one side of a 25 Fils Bahrain coin and (dashed) the other side of the same coin. The spectra are almost identical.

Figure 4 compares the LIBS spectra for three coins: a Saudi 10-Hallalah, a Euro 20 cent, and a token which is used for machine games. The results agree favorably with the NIST atomic spectra database. In comparing, there are some similarities between the three spectra; for example, all have peaks at the Fe 4307.9 Å. This means that all three samples have some iron. It is noted that the game token has more iron than the other (real) currencies.

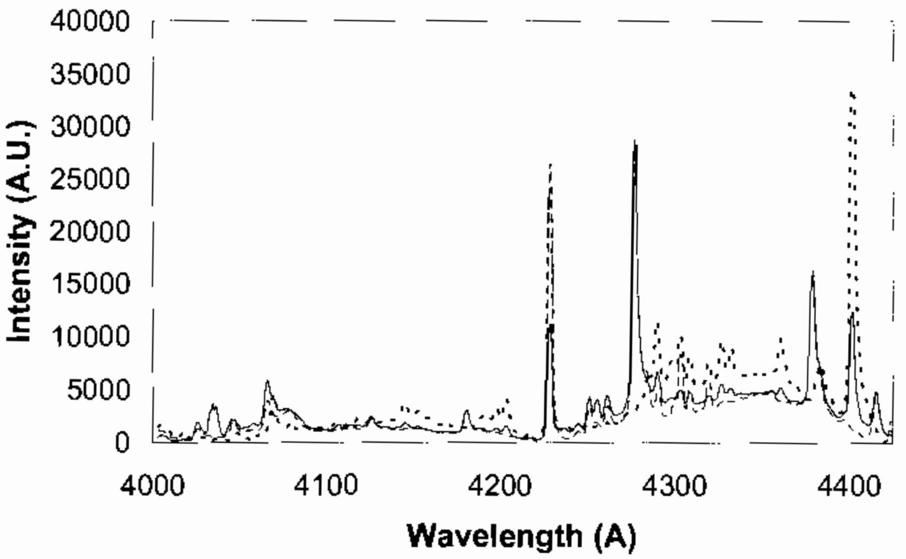

Fig. 4. LIBS spectra for (solid) a 10-Hallalah Saudi coin, (dashed) 20 cent Euro coin and (dotted) a game token, in the 4000-4425 Å region.

Nonetheless, under careful analysis, there are also distinet differenees between the spectra. For example, as can be seen at 4022.6, 4062.6, 4179.5, 4274.8, 4275.1, 4377.1, 4401.5 Å, the game token does not contain copper. The rcal currencies do contain copper.

Moreover, the Euro coin does not have the 4201.2 Ni peaks. Indeed, nickel has been limited, in the Euro currencics, to the two highest denominations of 1€ and 2€ Euro coins due to concerns that nickel possibly contribute to skin allergy (Fournier, 2003).

Figurc 5 compares the same three coius as in figure 4, but in a different region of the visiblc spectra; namely in the 5250-5550 Å region. Again, one comes to the same results. The common peaks at 5269.5 Å means that all these samples have some iron. Moreover, the game token does not produce a Cu peak at 5292.5 Å while the other currency coins do display peaks there. This proves that thc currency coins contain copper.

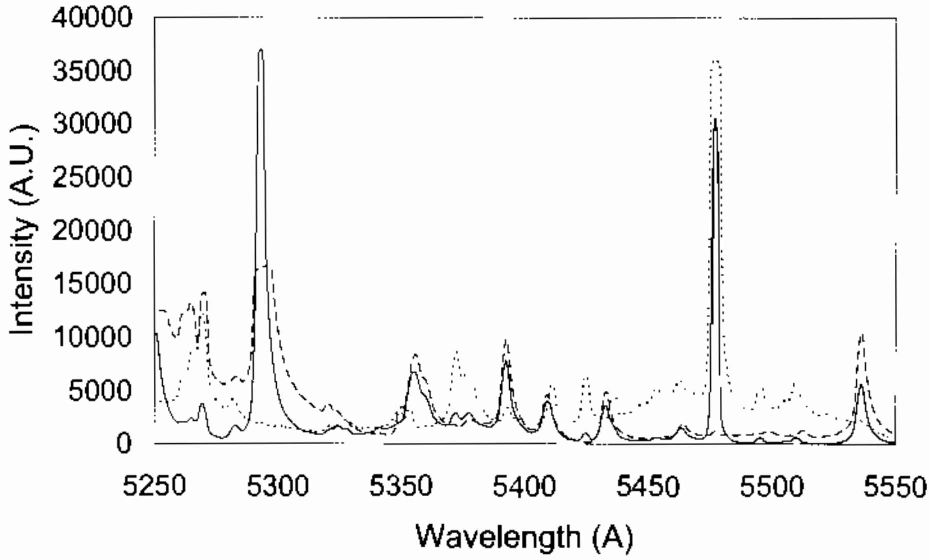

Fig. 5. LIBS spectra for the same coins of figure 4, in the 5250-5550 Å region.

The figure also shows that the Euro coin does not display peaks at 5424.6, 5475.4 5494.5 Å which arc the Ni peaks, supporting the fact that the 20 cent Euro coin does not contain nickel.

Unfortunately, the spectra of the Saudi 10-Hallalah and the Bahrain 25 Fils are very similar, and this is presumably because the two currencies use the same mixture of alloys. However, a detailed quantitative study may be able to distinguish between the two currencies. This is beyond the scope of this paper.

The detection system being a (non-gated) PDA, makes the sensitivity of detection much lower than a gated intensified charge coupled device (ICCD); hence, longer acquisition times are required. In thc experiments dcscribed above, the acquisition time was 30 seconds (i.e. 300 pulses), with laser energies of less than 2 mJ per pulse irradiating the rotating sample. This means that the average power was 0.02 watt and thc total energy absorbed by the sample during the 30 seconds is less 0.6 J. Therefore, the plasma formed during the experiment can not be more than a few tens of micrograms, and the testing is essentially "non-destructive". Figure 6 shows a photograph of thc coins after exposure to laser light. The coins look as good as new with no apparent damage to its appearance. Indeed, using gated ICCD, it is common for some systems to be able to analyze a sample in a single lascr shot (De Lucia *et al.*, 2003).

Fig. 6. a photograph of the four coins used in the experiments after 30 seconds of laser irradiation. The coins show no apparent destruction due to LIBS.

Conclusion

Different coins have been studied using LIBS which led to distinguishing between real coins on the one hand and a game token on the other. Moreover, the absence of nickel in Euro 20 cents has been confirmed. This leads to the conclusion that LIBS can be used for fast, precise, on-line, non-destructive testing (NDT) of coins. Hence, LIBS can be beneficial for the identification of currency and also for quality control in coins production.

It would be nice to study the accuracy of LIBS technique results, both qualitative and quantitative, under different photon energy, laser pulse energy, optical alignment of beam with the sample, and optical alignment of beam with the detection system. For detectors that can be gated, it would be nice to study the effects of delayed time detection (Fisher et al., 2001).

LIBS is conducive to interdisciplinary research, a concept very beneficial for academic research in Sandi Arabia. While the analysis method pertains basically to physics; it can be used to analyze geological rock samples which serve the Earth Sciences discipline. The Chemistry department faculty may benefit from LIBS analysis of plastics while Environmental Science and Engineering research can benefit from LIBS water contamination studies.

LIBS also emphasizes the potential role that basic science research has with the industry and presents one relevant method for industrial applications.

Acknowledgment

The support of King Fahd University of Petroleum and Minerals is gratefully acknowledged. The encouragement of professor M.A. Gondal, as well as the assistance of Mr. Abdullah Baziyad and Mr. Abdullah Al-Zahrani, is deeply appreciated.

References

Anzano, J.M., Villoria, M.A., Gornushkin, I.B., Smith, W.B. and **Winefordner, J.D.** *Canadian Journal of Analytical Sciences and Spectroscopy,* **47**(5), 134-140 (2002).

Buckley S.G., Johnsen H.A., Hencken K.R. and **Hahn D.W.** *Waste Management,* **20**, 455-462 (2000).

Carranza J.E., Fisher B.T., Yoder G.D. and **Hahn D.W.** *Spectrochimica Acta Part B,* **56**, 851-864 (2001).

De Lucia, F.C., Harmon, R.S., McNesby, K.L., Winkel, R.J. and **Miziolek, A.W.** *Applied Optics,* **42**(30), 6148-6152 (2003).

Fichet, P., Menut, D., Brennetot, R., Vors, E. and **Rivoallan A.** *Applied Optics,* **42**(30), 6029-6035 (2003).

Fisher, B.T., Johnsen, H.A., Buckley, S.G. and **Hahn, D.W.** *Applied Spectroscopy,* **55**, 1312-1319 (2001).

Fournier, P.G., Govers, T.R. and **Brun, A.** *Europhysics News,* 195-198, Sept./ Oct. (2003).

Kincade, K. *Laser Focus World,* 71-80, Aug. (2003).

Lee, Y.I., Song, K. and **Sneddon, J.** *Laser-Induced Breakdown Spectrometry,* Science Publishers, Inc. (2000).

Samek, O., Beddows, D.C.S., Kaiser, J., Kukhlevsky, S.V. Liska, M., Telle, H.H., Young, J. *Optical Engineering* **39**(8), 2248-2262 (2000).

Sattmann, R., Monch, I., Krause H., Noll, R., Couris, S., Hatziapostolou A., Mavromanolakis, A., Fotakis, C., Larrauri, E. and **Miguel, R.** *Applied Spectroscopy,* **52**(3), 456-461 (1998).

Tran, M., Smith, B.W., Hahn, D.W. and **Winefordner, J.D.** *Applied Spectroscopy,* **55**, 1455-1461 (2001).

Yamamoto, K.Y., Cremers, D.A., Ferris M.J. and **Foster, L.E.** *Applied Spectroscopy,* **50**(2), 222-233 (1996).

Yueh, F.Y., Sharma, R.C., Singh, J.P., Zhang, H. and **Spencer, W.A.** *Journal of the Air & Waste Management Association,* **52**, 1307-1315 (2002).

Weritz, F., Schaurich, D., Wilsch G., Wstmann, J. and **Wiggenhauser, H.** *Laser Induced Breakdown Spectroscopy as a tool for the characterization and sorting of concrete waste material in view of high-order re-use,* International Symposium (NDT-CE 2003).

Zolotovitskaya E.S., Glushkova, T.V. and **Blank A.B.** *Journal of Applied Spectroscopy,* **64**(3), 410-413 (1997).

دراسة لمكونات بعض العملات المعدنية باستخدام مطيافية البلازما المستحثة بالليزر غير المدمرة

د. زين بن حسن يماني

قسم الفيزياء ، جامعة الملك فهد للبترول والمعادن ، الظهران – المملكة العربية السعودية

البريد الإلكتروني: zhyamani@kfupm.edu.sa

المستخلص. في هذا البحث نستعرض كيف يمكن لمطيافيّة البلازما المستحثّة بالليزر (LIBS) أن تستخدم لتحليل مكوّنات عملات معدنية مختلفة. إن ممّا توصّلنا إليه هو أن LIBS وسيلة سريعة ودقيقة ومباشرة وغير مدمّرة لدراسة العملات المعدنيّة مما يؤهل هذا الأسلوب للتعرف على العملات وضبط جودتها.

في تجربتنا نستخدم ومضات المضاعف الثالث لليزر Nd-YAG فوق البنفسجية لإنتاج البلازما. نحلل الإشعاع الضوئي باستخدام محلل ونلتقط الإشارة باستخدام مصفوفة من اللاقطات الضوئيّة. قمنا بتحليل عيّنات من العملات السعودية واليورو والبحرينية وقطعة معدنيّة لإحدى مدن الألعاب فوجدنا أن عملية فحص العيّنة سريعة حيث تستغرق مجرد ٢٠ ثانية كما أنّه لا يظهر في الصور الفوتوغرافية الملتقطة أي تأثير بسبب الليزر حيث أن طاقته صغيرة (٣٠ مللي واط).

بتحليل المطياف وجدنا المكوّنات الأساسيّة للقطع المعدنيّة الأربع وتمكنا من التفريق بينها. إن LIBS وسيلة تحليل متقدّمة تفيد في مجالات بحثيّة عديدة. فعلماء الأرض يمكنهم أن يستفيدوا منها في تحليل الأحجار والكيميائيون يحللون بها المواد البلاستيكيّة وعلماء البيئة يحللون بها المخلّفات البيئية، وهي بهذا تزيد من التلاحم البحثي بين مجالات المعرفة المختلفة، هذا التلاحم الذي نحن بحاجة ماسّة إليه في المملكة العربيّة السعودية.