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Real-time analysis of mineral elements in oat using laser-induced breakdown spectroscopy

Echtzeit-Analyse von mineralischen Elementen in Hafer mittels Laser-Emissionsspektroskopie

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Summary

The aim of this research was to assess the contents of mineral elements in oat flour using laser-induced breakdown spectroscopy (LIBS) that was integrated with iterative discrete wavelet transform (IDWT) algorithm. By using LIBS in the IDWT domain, the effects of low-frequency baseline and high-frequency noise on LIBS signals were greatly suppressed. The IDWT-LIBS is thus capable of accurately quantifying mineral elements in the presence of an uncontrolled matrix of oat flour. To validate the IDWT-LIBS method, oat samples with various Ca, Mg, and K concentrations were measured, and their characteristic signals were linearly dependent on their concentrations, with an R^2 being above 0.98. The limits of detection of these elements were determined as 20 ppm. The results obtained by LIBS were in reasonable agreement with those obtained by inductively coupled plasma optical emission spectroscopy (ICP-OES), indicating that IDWT-LIBS is a promising tool for the real-time quantification of mineral elements in oat flour samples.

Keywords: LIBS, oat flour, real-time analysis, mineral elements, IDWT, ICP-OES

Introduction

Cereal grains represent an essential source of nourishment and has been considered as one of the most important sources of calories for humans for a long time(Awika, 2011). Cereal groups provide appropriate amounts of essential nutrients and form an important part of a balanced diet (Dewettinck et al., 2008; Poutanen, 2012). About 70 % of the recommended daily intake of mineral elements can be satisfied by daily consumption of food products containing 200 g of wholemeal flour (Hussain et al., 2010).

Among cereals, oats are considered as a good source of fibre and have a well-balanced nutritional composition, such as high percentage of lipids, especially unsaturated fatty acids, minerals, vitamins, and phytochemicals (Head et al., 2010). Due to their beneficial health effects, such as lowering blood glucose and cholesterol levels, they have gained considerable interest as a health food (Rasane et al., 2015; Whitehead et al., 2014).

Among these nutrients, mineral elements play vital roles. The daily consumption of mineral elements is necessary for the proper functioning of the human body. They are structure-forming elements (macro elements) and participate in the regulation of biochemical processes (microelements) (Barczak et al., 2006). For example, potassium (K)decreases risks of stroke, lowers blood pressure, protects against loss of muscle mass, preserves bone mineral density, and reduces the formation of kidney stones. It also plays an important role in the ß-cells of the endocrine pancreas for insulin secretion. In the past years, the collective evidence from epidemiological studies suggests that lower intake of potassium or serum potassium levels are associated with a higher risk for type 2 diabetes (Chatterjee et al., 2011). It is considered as an essential mineral that participates in intracellular osmolality and plays an important role in the resting membrane potential (Ekmekcioglu et al., 2016). While calcium (Ca) is the richest mineral in the body and it is responsible for developing and maintaining healthy bones and teeth (Fairweather-Tait & Cashman, 2015). Ca also reduces the risk of cardiovascular disease by decreasing the level of cholesterol in the blood (Bostick et al., 1999). Magnesium (Mg) is responsible for the activation of an enzyme alkaline phosphatase that forms new calcium crystals in bones, and many other enzymes function in the replication of DNA and the synthesis of RNA. It is also involved in bone metabolism, muscle and nerve function, control blood glucose, and also regulates blood pressure (Fairweather-Tait & Cashman, 2015; Rodríguez-Morán et al., 2012). All these elements have their own unique roles and functions and are required by the body in small amounts for a variety of different functions.

A number of traditional laboratory methods are used to quantify mineral elements present in different kinds of food, and some of them are officially approved by different organizations such as AOAC International, ISO and the European Nordic Committee (NMKL). These traditional methods include flame atomic absorption spectrometry (FAAS) (Jākobsone et al., 2015; AOAC **985.35,** AOAC **999.10,** NMKL 161:1998), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Yang et al., 2012; AOAC **2011.14,** ISO/CD 15151), inductively coupled plasma optical emission spectrometry (ICP-OES) (Kan, 2015; ISO 11885: 2007, AOAC 984.27), and atomic absorption spectrometry (AAS) (Ciolek et al., 2012; AOAC **972.25**). However, a large amount of sample is required for these methods and a pre-treatment procedure is generally necessary, which converts the solid sample into an aqueous homogeneous solution. In addition to the time-consuming procedure, a strictly controlled laboratory environment is also required to reduce contamination. Moreover, most of the instruments and equipment used in these techniques are very expensive, increasing the overall cost. Therefore, the development of a rapid and accurate method for minerals quantification in cereals has become highly desirable.

Laser-induced breakdown spectroscopy (LIBS) offers a potential alternative. It has many advantages over other existing analytical techniques, such as minimal or no sample preparation, high throughput, small sample quantity, and multi-elemental detection capability (Ferreira et al., 2010). LIBS analyses a sample by detecting the emission of plasma generated by laser ablation, providing an immediate spectral fingerprint of its elemental compositions. In LIBS equipment, a laser pulse with high power density is focused on a target material for less than a nanosecond, resulting in a high-temperature plasma via vaporizing a small portion of that target (Zheng et al., 2014). LIBS offers a strong capability of rapidly detecting elemental contents in different kinds of samples, such as solid, liquid, gas, or aerosol specimens(Chen et al., 2020; Eseller et al., 2010; Zhang et al., 2019).

In the present study, we demonstrated that LIBS can be used for quantifying of mineral elements such as Ca, Mg, and K in oat. The signal intensities of the atomic emission lines related to these elements were linearly proportional to their concentrations. After obtaining the calibration curves, the concentrations of minerals in raw oats as well as those with additions were also obtained, and the predicted concentrations agreed very well with the actual values. The results obtained by LIBS spectroscopy also agreed very well with those provided by ICP-OES analysis, demonstrating that LIBS is a simple and rapid analytical technique for minerals quantification in cereals and will find wide applications in food industry.

Materials and methods

Sample preparation for LIBS measurements

A total of 35 samples of five different brands of oat were used in the present work. The packaged oats of different brands were purchased from a local market in Tianjin, China. The grains were ground into powder using grinder (Midea, Foshan, China); the powder was then sieved using a mesh with a mesh size of 75 µm. The powdered sample was made into pellets by a hydraulic machine. For each sample, 1 g of powder was placed into the stainless steel die with a diameter of 12 mm and pressed at 30 tons of force for 2 min. The resulted pellets had a thickness of 5 mm and a diameter of 12 mm. To study the dependence of signal intensity on Ca, Mg and K concentrations, different amounts of potassium, ranging from 5 to 50 mg per pellet, and calcium and magnesium, ranging from 2 to 15 mg per pellet, were also added into the powder prior to pellet preparation. To make sure that the addition is uniform, potassium chloride, calcium chloride, and magnesium sulphate were mixed with the oat powder gently for 1 minute using a glass rod, followed by sonication for 5 minutes. All experiments were carried out with three independent sample preparations to give statistical results.

ICP-OES analysis

In this work, we used ICP-OES as a reference method to validate the performances of LIBS. To prevent contamination during sample preparation, all glassware and polypropylene flasks were washed and soaked in 10 % (v/v) HNO_3 for 24 h, after which they were rinsed with deionized water and dried naturally. To prepare the samples for ICP-OES, 100mg of oat sample was placed in a Teflon microwave vial; 6.0 mL of nitric acid and 1.0 mL of ultra-pure water were added. A cavity microwave oven (TOPEX+, Shanghai, China) was used for sample decomposition. All experiments were carried out with three replicates.

The samples were analysed using a PQ9100 (Analytik Jena AG, Germany) inductively coupled plasma optical emission spectrometer (ICP-OES). The sample introduction system consisted of a concentric nebulizer with a double-pass cyclonic spray chamber. The settings used in this work were as follows: 1.2 kW radio frequency power, 12 L min^{-1} plasma flow rate, 0.5 L min^{-1} nebulizer flow rate, 0.5 L min^{-1} auxiliary flow rate, and 0.5 mL min^{-1} sample flow rate.

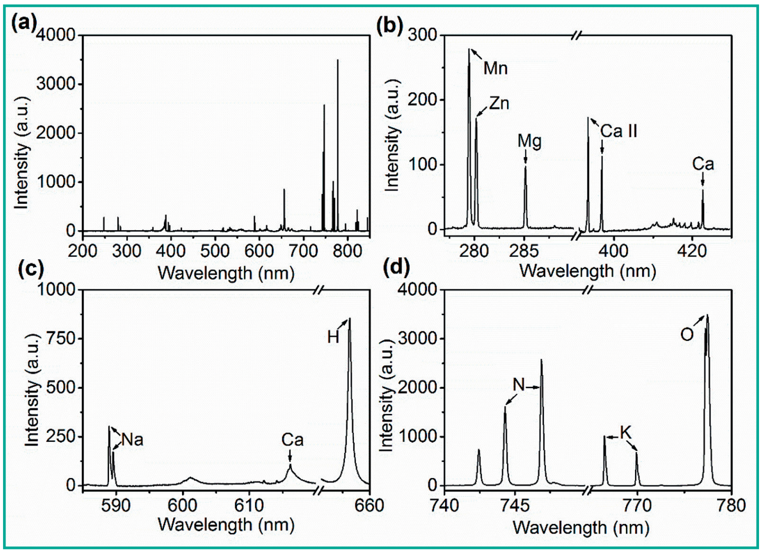

FIGURE 2: *(a) A typical LIBS spectra of oat samples. (b–d) The spectrum display in different wavelength ranges for better visualization.*

LIBS analysis

Figure 1 shows a schematic diagram of the LIBS setup, which consisted of a laser source, focusing and collection optics, a translation stage, and a multi-channel spectrometer. A Nd: YAG laser source (LIBSLAS200MJ, Big Sky Laser Technologies) was used to generate plasma emission in the oat samples. The Q-switched Nd: YAG laser was operated at the fundamental wavelength of 1,064 nm. The pulse energy was 50 mJ, with the pulse duration and repetition rate being 9.5 ns and 10 Hz, respectively. The laser beam was focused onto the pellet's surface by a lens with a focal length of 75 mm to produce ionized plasma. A 7-channel spectrometer (Ocean Optics, Florida, US) was used to record the plasma emission spectrum. The spectrometer had a spectral resolution of 0.1 nm (FWHM) and covered a wavelength range of 200 to 800 nm.

For each pellet, 30 locations on its surface were randomly selected for LIBS measurement to account for the non-uniformity of the mixtures. A translation stage was used to move the sample without altering the laser focusing on the sample's surface. All experiments were carried out with three replicates (n=3) at each concentration of Ca, Mg and K. As a result, a total of 90 LIBS spectra were collected at each concentration, the spectra were then averaged to take in account the fluctuations in laser pulse energy, the roughness of the sample surface as well as the non-uniformity of the mixtures.

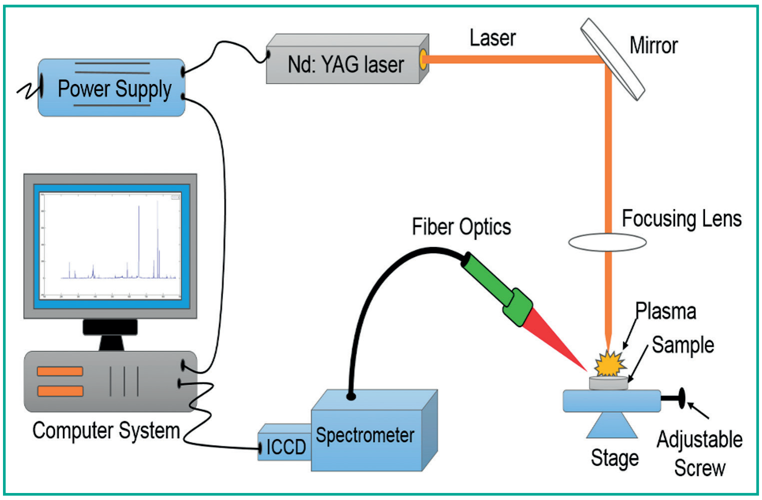

FIGURE 1: *Optical setup of LIBS System for the analysis of mineral elements in oat.*

Iterative discrete wavelet transform (IDWT)

To remove the low-frequency baseline and the high-frequency instrumental noise in the LIBS spectral data, an iterative discrete wavelet transform (IDWT) algorithm was used (Galloway et al., 2009; Tan et al., 2017). Sym5 was used as the wavelet basis, and all spectra were firstly decomposed into 9-level components that contain 8 detail components and 1 approximate component. The negative amplitudes of the spectra were removed, and the lowest and highest frequency components were discarded. The resulted spectra were used as the input of the next iteration, and this process was repeated until the arithmetic square root of the squared sum of the differential spectrum between two successive iterations was less than 0.1% of the spectrum's total energy. The IDWT algorithm overcomes the drawback of a traditional DWT that usually produces signal distortion and negative amplitudes (Zhang et al., 2019).

Results and discussion

As we have discussed above, mineral elements such as Ca, Mg, and K are important for human health, this research is therefore focused on the quantitative analysis of these elements in oats. Figure 2(a) represents a typical LIBS spectrum of an oat sample without the addition of these elements. The spectrum was averaged over 90 laser shots, and the baseline and high-frequency noise had been removed by IDWT, as detailed in Materials and Methods. The different wavelength ranges of the spectrum are also shown in Fig. 2(b–d) for better visualization, in which several mineral elements such as K, Ca, Mg, Mn, Na, and Zn, display observable plasma emissions. These elements were detected simultaneously by taking the advantage of that the atomic emissions have very narrow spectral widths and a high-resolution (<0.1 nm) spectrometer was used for LIBS recording.

To measure the amounts of these elements presented in oats, the relationship between the LIBS intensities of these elements and their concentrations must be determined. For this purpose, we measured the LIBS of the oat samples by adding different amounts of Ca, Mg, and K. The spectra of the oat samples with different amounts of Ca, Mg, and K addition are shown in Fig. 3. As can be seen, the higher are the concentrations of Ca, Mg, and K, the stronger are the peak intensities at their specific wavelengths. To quantitatively describe the dependences of the LIBS spectral signals on the elemental concentration, we calculated the peak intensities of their characteristic emission lines. Since these element usually have more than one emission lines, the lines that have highest sensitivities and linearity were regarded as the most effective spectral lines for elemental quantification. According to the Atomic Spectra Database (ASD) of National Institute of Standards and Technology (NIST), the peaks located at 422.673 nm, 285.213, nm and at 766.57 nm are assigned to calcium, magnesium, and potassium, respectively. These peaks were then selected for quantifying the calcium, magnesium, and potassium contents in oats.

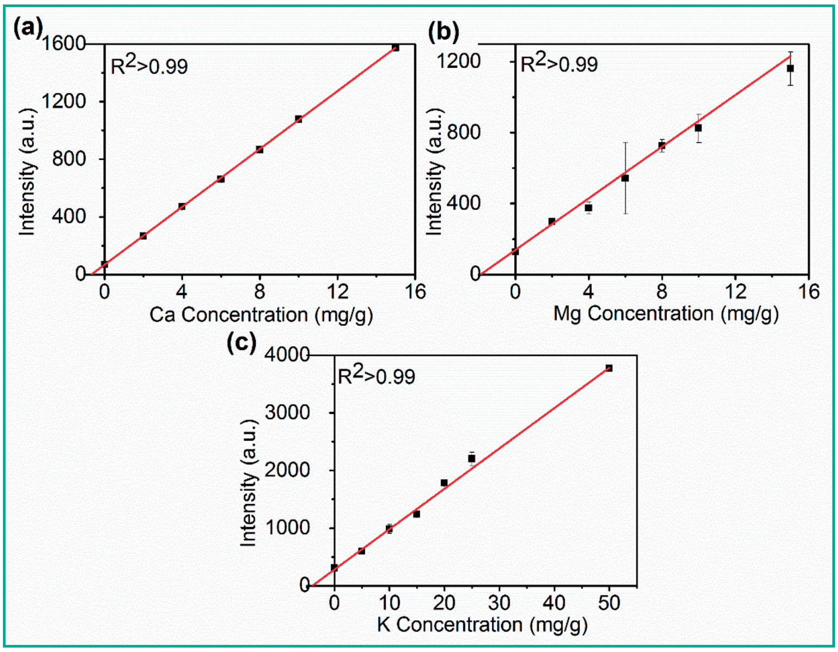

FIGURE 4: *(a) Peak intensity at 422.673 nm as a function of the calcium concentrations, (b) Peak intensity at 285.213 nm as a function of the magnesium concentrations, and (c) Peak intensity at 766.57 nm as a function of the potassium concentrations.*

Figure 4 shows the peak intensities at these wavelengths as a function of the added calcium, magnesium, and potassium concentrations. Obviously, the emission intensities of these specific lines were linearly proportional to the added concentrations, demonstrating that LIBS is a quantitative analytical method for mineral elements characterization. The R^2 of the linear regression was higher than 0.98. The linear fitting of the experimental data is not crossing the origin, indicating that the raw oat powder contains Ca, Mg and K, and their concentrations can be determined by the intercepts of their regression lines on the negative x-axis (Haider et al., 2010).

The concentrations of Ca, Mg, and K were also determined by ICP-OES to validate the LIBS method, and the experimental data are listed in Table 1. As shown, the results obtained by LIBS were in good agreement with those obtained by ICP-OES, proving that LIBS technique is a good alternative to ICP-OES for the determination of mineral elements in oat flour samples without sample pre-treatment procedures. The limits of detection (LOD) of these elements were also determined by using the calibration curve method. It is defined as the minimum amount of analytes that can be detected. The LODs of Ca, Mg and K in oat powder can be calculated using the following equation(Guideline, 2005),

$$LOD = (3.3S_a)/s,$$

where S_a is the standard deviation of background noise near the peaks and s represents the slopes of the calibration curves. By using this equation, the LODs of these mineral elements were determined as 20 ppm.

With the calibration curves in hand, the LIBS system then can be used for quantifying the concentrations of mineral elements in different oat samples. We prepared blind samples with various mineral elements concentrations, acquired their LIBS spectra, and then predicted their concentrations using the calibration curves. Figure 5 shows the concentrations of Ca, Mg, and K predicted by LIBS spectroscopy versus their actual concentrations (scatters). The actual concentrations are also plotted as a function of themselves (red solid lines) to show the differences between predicted and actual values. It is obviously that all the scatters almost fall on the lines; the minor differences

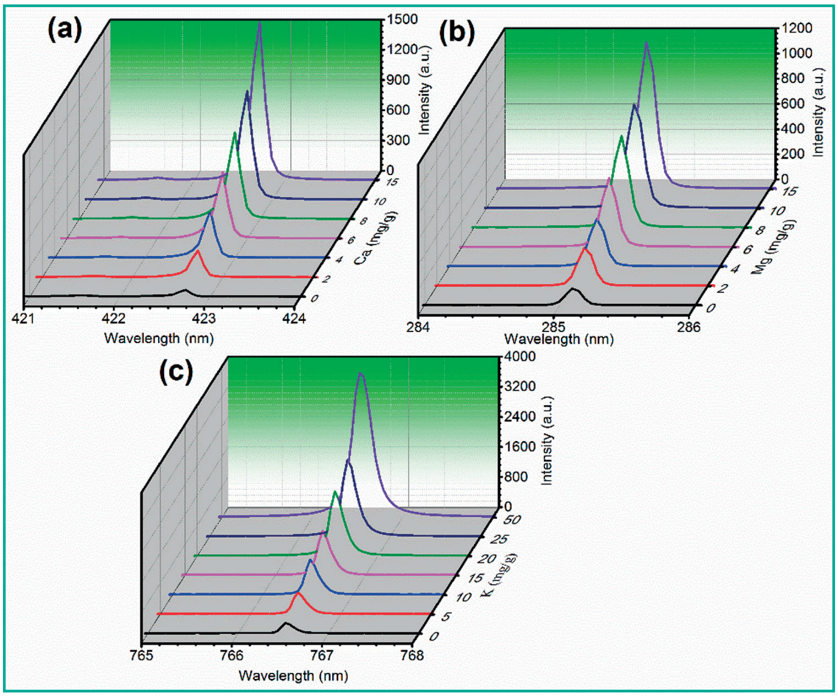

FIGURE 3: *LIBS spectra of oat samples at different added concentrations of (a) calcium, (b) magnesium, and (c) potassium.*

between them may be due to the errors in the sample preparation and the data acquisition. It indicates that the predicted concentrations of Ca, Mg, and K are very close to their actual values. The results suggest that LIBS spectroscopy can be used as an alternative analytical method to the traditional methods for rapidly quantifying the concentrations of mineral elements presented in oats.

Conclusion

In this study, LIBS was implemented for the quantification of calcium, magnesium, and potassium as well as other mineral elements in oat samples. It is found that different oat brands used in this study contain a large number of mineral elements. It is also observed that the effects of low-frequency baseline and high-frequency noise on LIBS signals were greatly suppressed by using LIBS in IDWT domain. The intensities of the characteristic emission lines related to mineral elements were linearly proportional to their concentrations. The concentrations of Ca, Mg, and K determined from the calibration curves were in a good agreement with those obtained by the ICP-OES measurements. The LIBS spectroscopy was then used for the measurement of blind oat samples, and the predicted concentrations of the mineral elements were also very close to their actual values. It should be noted that the calibration procedure has to be done with each LIBS system when applied to quantification of mineral elements in oats. The limit of detection of the proposed model was determined as 20 ppm, which is also appropriate for the determination of the concentrations of Ca, Mg, and K in the commercially available cereals. The results reported here show that LIBS is a very promising technique for mineral quantification in oat and other cereals and can be used as an alternative to other laboratory analytical methods in the food industry.

TABLE 1: Ca, Mg, and K concentrations in different brands of oat, as determined by ICP-OES and LIBS.

Sample		ICP-OES			LIBS	
	Ca (mg/kg)	Mg (mg/kg)	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	K (mg/kg)
Brand 1	553±76a	914±168	3103±425	520±11	1509±14	3449±136
Brand 2	307±3	670±21	3016±38	302±23	811±165	2762±278
Brand 3	356±5	801±4	3514±44	386±21	835±80	4267±230
Brand 4	657±110	926±18	3437±60	689±31	1352±180	3567±189
Brand 5	669±14	1188±20	3481±56	676±21	1897±76	3999±257

[a] All values are means ± SD of data

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Authors Contributions

Naqash Ali, Yiwen Ma and Yabing Xiao designed experiments, Naqash Ali performed experiments and prepared manuscript, Naqash Ali, Zhixuan Huang, Jing Zong and Lei Wang analyzed and processed data, and Pengfei Zhang and Da Chen supervised project.

Conflict of interest

There are no conflicts of interest to declare in this manuscript.

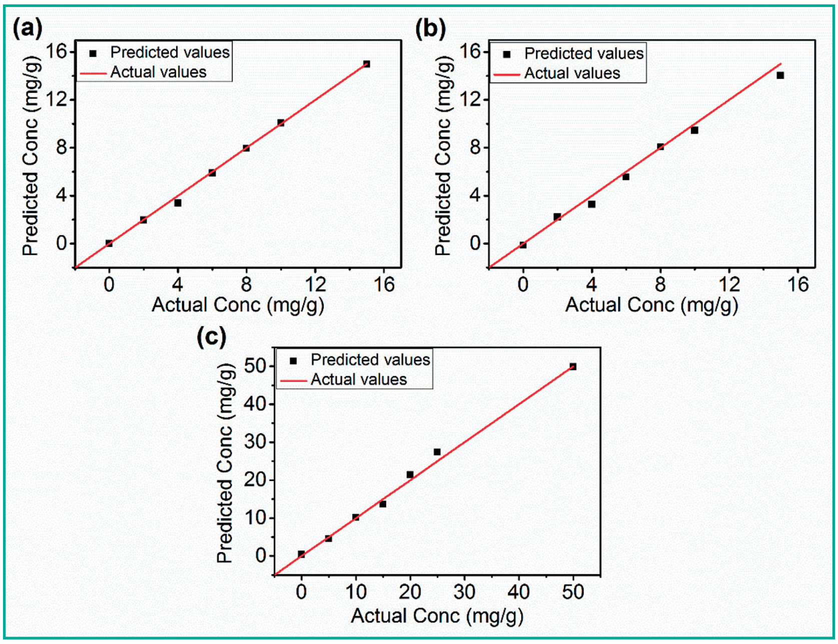

FIGURE 5: *Concentrations of calcium (a), magnesium (b), and potassium (c) predicted by LIBS spectroscopy in oat samples vs their actual concentrations (scatters).The actual concentration are also plotted as a function of themselves for comparisons (red lines).*

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