



Analytical Methods

Authentication of vegetable oils by confocal X-ray scattering analysis with coherent/incoherent scattered X-rays



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ABSTRACT

This paper presents an alternative analytical method based on the Rayleigh to Compton scattering intensity ratio and effective atomic number for non-destructive identification of vegetable oils using confocal energy dispersive X-ray fluorescence and scattering spectrometry. A calibration curve for the Rayleigh to Compton scattering intensity ratio and effective atomic number was constructed on the basis of a reliable physical model for X-ray scattering. The content of light elements, which are “invisible” using X-ray fluorescence, can be calculated “by difference” from the calibration curve. In this work, we demonstrated the use of this proposed approach to identify complex organic matrices in different vegetable oils with high precision and accuracy.

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1. Introduction

There is growing interest in the chemical composition of vegetable oils for the assessment of quality, and authentication of edible oils is of great importance for both commercial value and health. Many methods and techniques have been reported for the assessment of vegetable oils, including capillary electrophoresis (Isabella, Maria, Leandros, & Markus, 2015; María, Aarón, María, Ernesto, & José, 2011), gas chromatography (Zhang et al., 2014; Jabeur et al., 2014), high-performance liquid chromatography (Jabeur et al., 2014; Zhao, Chen, Fang, Li, & Zhao, 2013), high performance countercurrent chromatography (Hamid et al., 2015), energy dispersive X-ray fluorescence combined with principal components analysis (Bortoleto, Pataca, & Bueno, 2005). Most of these methods require pre-treatment of sample, such as solubilization in solvents, extraction, etc. Spectroscopic techniques are ideal for the assessment of vegetable oils because they are simple, cost-effective, rapid and non-destructive. Many spectroscopic methods for analysis of edible oils have been reported, for instance, near infrared spectra (Mezghani et al., 2015), nuclear magnetic resonance spectroscopy (Covadonga, Ángel, Beatriz, & Andrés, 2014), and fluorescence spectroscopy (Maurizio, Laura, & Chiara, 2005;

Sikorska, Górecki, Khmelinskii, Sikorski, & Kozioł, 2005; Guzmán, Baeten, Pierna, & García-Mesa, 2015). Among these spectroscopic techniques, fluorescence spectroscopy is one of the most promising techniques of increasing importance in complex food analysis. Among the benefits of fluorescence spectroscopy are enhanced selectivity compared with other spectroscopic methods, high sensitivity to a wide array of potential analytes and, in general, reduced consumption of reagents and extensive sample pre-treatment (Oldham, McCarroll, McGown, & Warner, 2000).

Energy dispersive X-ray fluorescence (EDXRF) is a well-established multi-element and nondestructive fluorescence spectroscopy analytical technique that is widely reported in the literature for the qualitative and/or quantitative determination of trace, minor, and major elements in a large variety of matrices (Akiko, Akiko, & Izumi, 2014; Da-Col, Bueno, & Melquiades, 2015). Nevertheless, the qualitative and/or quantitative determination of trace or ultratrace levels of higher-Z elements in organic matrices is difficult, due to the low-Z “dark matrix”, which enhances the matrix absorption effects and gives rise to a high spectral background (Pouzar, Černohorský, & Krejčová, 2001). Furthermore, determination of low-Z elements by conventional X-ray fluorescence (XRF) is a difficult task because of the low fluorescence yields of their characteristic X-ray analytical lines, strong absorption of these X-ray lines in air atmosphere, sample matrix as well as spectrometer components, high spectral background in this region, especially in EDXRF geometry, low fluorescence yield

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of low-Z elements, and low efficiency of the detector (Akiko et al., 2014; Magalhães, Bohlen, Carvalho, & Becker, 2006). Total reflection X-ray fluorescence (TXRF), because of its excellent excitation, detection, and low background geometry has detection limits several orders better than the EDXRF and has a better potential for determination of low Z elements (Magalhães et al., 2006; Carvalho, Magalhães, Becker, & Bohlen, 2007). However, the few alternative methods that are used to directly measure the low-Z elements involve sophisticated instrumentation, like synchrotron radiation or vacuum chambers (Strelí et al., 2003; Misra et al., 2010; Dhara et al., 2014). In these cases, to achieve a satisfactory detection limit, the irradiation times are relatively long, but even then the precision and accuracy are increased significantly.

Rayleigh and Compton scattered lines can be found together with the fluorescent lines in XRF. These two scattered radiations are normally considered as drawbacks, except for the cases when they are used to correct for matrix effects (Dyck & Grieken, 1980). Moreover, when determining the content of low-Z elements in materials, the use of these two scattered radiations could be advantageous (Da-Col et al., 2015; Kaniu, Angeyo, Mwala, & Mwangi, 2012; Patterson, Obrey, Hamilton, & Havrilla, 2012; Bortoleto et al., 2005). The total mass absorption coefficient consists of a mass scattering coefficient and a photoelectric coefficient. The photoelectric coefficient is always higher than the mass scattering coefficient in the X-ray domain, and changes in the high MeV-region (Berger et al., 2010). Because the total mass absorption coefficient decreases with decreasing Z, for low-Z elements, the mass scattering coefficient becomes an increasingly larger part of the total mass absorption coefficient and the photoelectric coefficient becomes smaller, which is, of course, one of the problems with fluorescence. Therefore, the scatter regions can be more quantitatively informative for quantitative analysis of low-Z elements. Even compounds or mixtures without any characteristic X-ray fluorescent lines can still be analyzed. For instance, Dwiggins proposed the method of the use of intensity ratio of coherent to incoherent scattering of X-rays to determine hydrogen and carbon in hydrocarbons, particularly petroleum, and in a matrix containing additional elements (Dwiggins, 1961). This method shows a high precision and accuracy in the determination of low-Z elements. It relies on the fact that both coherent and incoherent scattered peak intensities are sensitive functions of sample matrix compositions. Therefore, organic samples provide very intense scattering processes.

It has long been known that elements of very low atomic number produce much Compton scattering, while elements of higher atomic number produce a larger proportion of Rayleigh scattering. Therefore, the intensity ratio of the Rayleigh to Compton scattering (R/C) should be sensitive to small changes in the composition of samples. R/C is not directly dependent on the physical density of materials, but on Z. For a compound matrix (of light, non-measuring elements), the concept of effective atomic number (Z_{eff}) can be employed to replace it by a single “virtual” element with the same impact upon the analyte line. The Z_{eff} helps visualizing many physical characteristics of a sample with a single number, and has been efficiently applied to the analysis of liquids, biological samples, powders, and polymers where the non-measuring elements were unknown and could not be easily analyzed by conventional EDXRF and/or TXRF. The Z_{eff} is an intrinsic characteristic of a sample, and due to this unique advantage, a large number of literatures have reported the use of the R/C method for measuring Z_{eff} of samples (Dwiggins, 1961; Kunzendorf, 1972; Hodoroaba & Rackwitz, 2014; Campbell et al., 2013; Antoniassi, Conceição, & Poletti, 2014). For example, Kunzendorf utilized the R/C method for a quick determination of the Z_{eff} of rock powders (Kunzendorf, 1972). Hodoroaba and Rackwitz studied the R/C in XRF for improving the elemental composition analysis (Hodoroaba & Rackwitz,

2014). Campbell et al. proposed a refined R/C method for using on the Mars Science Laboratory alpha particle X-ray spectrometer (Campbell et al., 2013). Antoniassi et al. presented a preliminary computational study of the R/C tomography and applied it to breast cancer diagnosis (Antoniassi et al., 2014).

The main scope of this paper was to find an alternative method with high precision and accuracy for identification of different vegetable oils. In vegetable oils, as in organic matrices, the main chemical compositions are light elements, namely carbon, hydrogen, and oxygen. The low fluorescence yields of these light elements do not favor a reliable XRF analysis. However, if the functional relationship between the R/C and Z_{eff} of samples were well understood, then this could supply valuable information on the composition of the light elements. Hence, the R/C resulting from X-ray scattering can be used to identify the different vegetable oils.

In this paper, we used the confocal energy dispersive X-ray fluorescence and scattering (EDXRFS) spectrometer based on polycapillary X-ray lens to analyze vegetable oils. The confocal EDXRFS spectrometer was based on a polycapillary focusing X-ray lens (PFXRL) in the excitation channel, and a polycapillary parallel X-ray lens (PPXRL) in the detection channel. A probing volume was created by the overlap of the output focal spot of the PFXRL and the input focal spot of the PPXRL. Only the fluorescence and scattered radiation from this probing volume can be detected. X-ray scattering spectra of different vegetable oils were obtained non-destructively with this confocal EDXRFS spectrometer. Finally, the corresponding Z_{eff} values of different vegetable oils were obtained by calculating the R/C of each using the area of Rayleigh and Compton scattering. Subtle differences between the vegetable oils, which were invisible in XRF spectra, were revealed based on the evaluated Z_{eff} .

2. Material and methods

2.1. Theoretical basis of X-ray scattering

When matter is irradiated by a beam of X-rays, photoelectric absorption, coherent (or elastic, or Rayleigh) scattering and incoherent (or inelastic, or Compton) scattering may occur. The intensities of Rayleigh (I_R) and Compton (I_C) scattered from the matter at a scattering angle θ detected by the detector are related to the corresponding peak areas in the measured spectrum and can be written, respectively, as:

$$I_R = I_0 k \frac{d\sigma_{Ra}}{d\Omega} \frac{1 - \exp[-\rho d \mu(E_0)(\csc\varphi_1 + \csc\varphi_2)]}{\mu(E_0)(\csc\varphi_1 + \csc\varphi_2)} \quad (1)$$

$$I_C = I_0 k \frac{d\sigma_{Co}}{d\Omega} \frac{1 - \exp[-\rho d (\mu(E_0)\csc\varphi_1 + \mu(E_{Co})\csc\varphi_2)]}{\mu(E_0)\csc\varphi_1 + \mu(E_{Co})\csc\varphi_2} \quad (2)$$

where I_0 is the intensity of incident photons and k is a constant corresponding to the given geometric parameters of the confocal instrument and the detector efficiency. φ_1 and φ_2 correspond to the incident and exit angles, respectively. $\frac{d\sigma_{Ra}}{d\Omega}$ and $\frac{d\sigma_{Co}}{d\Omega}$ correspond to the Rayleigh and Compton differential scattering cross-sections, respectively. $\mu(E_0)$ and $\mu(E_{Co})$ correspond to the mass absorption coefficient at energies E_0 and E_{Co} , respectively. The relationship between E_0 and E_{Co} is the well-known Compton kinematic equation:

$$E_{Co} = \frac{E_0}{1 + (E_0/m_0c^2)(1 - \cos\theta)} \quad (3)$$

Based on Eqs. (1) and (2), the R/C has the following form:

$$R/C = \frac{I_R}{I_C} = \frac{\frac{d\sigma_{Ra}}{d\Omega} \frac{1 - \exp[-\rho d \mu(E_0)(\csc\varphi_1 + \csc\varphi_2)]}{\mu(E_0)(\csc\varphi_1 + \csc\varphi_2)}}{\frac{d\sigma_{Co}}{d\Omega} \frac{1 - \exp[-\rho d (\mu(E_0)\csc\varphi_1 + \mu(E_{Co})\csc\varphi_2)]}{\mu(E_0)\csc\varphi_1 + \mu(E_{Co})\csc\varphi_2}} \quad (4)$$

When choosing available E_0 and θ , the mass attenuation coefficients, $\mu(E_0)$ and $\mu(E_{Co})$, are roughly equal, which can be validated from the XCOM database (Berger et al., 2010). Therefore, the R/C can be written as:

$$R/C = \frac{I_R}{I_C} = \frac{d\sigma_{Ra}}{d\Omega} / \frac{d\sigma_{Co}}{d\Omega} \quad (5)$$

The differential scattering cross-sections for Rayleigh and Compton scattering are (Hubbell et al., 1975):

$$\frac{d\sigma_{Ra}}{d\Omega} = \frac{d\sigma_T}{d\Omega} F^2(\chi, Z) \quad (6)$$

$$\frac{d\sigma_{Co}}{d\Omega} = \frac{d\sigma_{KN}}{d\Omega} S(\chi, Z) \quad (7)$$

where $\frac{d\sigma_T}{d\Omega}$ and $\frac{d\sigma_{KN}}{d\Omega}$ are the Thomson and Klein-Nishina cross sections, respectively. $F(\chi, Z)$ constitutes the scatter form factor of element Z , and $S(\chi, Z)$ is the incoherent scattering function. χ is the momentum transfer and is related to the scatter angle θ and E_0 by:

$$\chi = \frac{E_0}{hc} \sin\left(\frac{\theta}{2}\right) \quad (8)$$

where h and c are the Planck's constant and the speed of light in vacuum, respectively. For compounds, they contain various elements, and thus, Eqs. (6) and (7), can be written, respectively, as:

$$\frac{d\sigma_{Ra}}{d\Omega} = \frac{d\sigma_T}{d\Omega} \sum_{i=1}^n a_i^{at} F^2(\chi, Z_i) \quad (9)$$

$$\frac{d\sigma_{Co}}{d\Omega} = \frac{d\sigma_{KN}}{d\Omega} \sum_{i=1}^n a_i^{at} S(\chi, Z_i) \quad (10)$$

where a_i^{at} is the atomic percentage of the i th element. Therefore, the R/C can be expressed as:

$$R/C = \frac{I_R}{I_C} = \frac{d\sigma_{Ra}}{d\Omega} / \frac{d\sigma_{Co}}{d\Omega} = \frac{\frac{d\sigma_T}{d\Omega} \sum_{i=1}^n a_i^{at} F^2(\chi, Z_i)}{\frac{d\sigma_{KN}}{d\Omega} \sum_{i=1}^n a_i^{at} S(\chi, Z_i)} \quad (11)$$

If substituting a compound matrix by a single element of Z_{eff} , then, Eq. (11) can be simplified as the following form:

$$R/C = \frac{I_R}{I_C} = \frac{d\sigma_{Ra}}{d\Omega} / \frac{d\sigma_{Co}}{d\Omega} = \frac{\frac{d\sigma_T}{d\Omega} F^2(\chi, Z_{eff})}{\frac{d\sigma_{KN}}{d\Omega} S(\chi, Z_{eff})} \quad (12)$$

The Thomson and Klein-Nishina cross-sections (Hubbell et al., 1975) are then:

$$\frac{d\sigma_T}{d\Omega} = \frac{r_e^2}{2} (1 + \cos^2\theta) \quad (13)$$

$$\frac{d\sigma_{KN}}{d\Omega} = \frac{r_e^2}{2} \frac{1}{[1 + k(1 - \cos\theta)]^2} [1 + \cos^2\theta + \frac{k^2(1 - \cos\theta)^2}{1 + k(1 - \cos\theta)}] \quad (14)$$

where r_e is the classical electron radius and k is equal to $E_0/m_0c^2 \cdot \frac{d\sigma_T}{d\Omega}$ and $\frac{d\sigma_{KN}}{d\Omega}$ have quite a simple dependence only on E_0 and θ , and can be easily calculated. In particular, if E_0 is much smaller than m_0c^2 (i.e., $k \ll 1$), then $\frac{d\sigma_T}{d\Omega}$ is approximately equal to $\frac{d\sigma_{KN}}{d\Omega}$. Thus, Eq. (12) can be written as:

$$R/C = \frac{I_R}{I_C} = \frac{d\sigma_{Ra}}{d\Omega} / \frac{d\sigma_{Co}}{d\Omega} = \frac{F^2(\chi, Z_{eff})}{S(\chi, Z_{eff})} \quad (15)$$

From Eq. (15), it is found that the R/C has a specific dependence on the Z_{eff} .

In Fig. 1a, a plot is presented of the mass scattering coefficients σ_{Ra} and σ_{Co} for the chosen Mo K_α (17.443 keV) radiation at the scattering angle $\theta = 90^\circ$. The Compton scattering coefficient decreases only weakly with Z , whereas the Rayleigh scattering coefficient is a strongly increasing function of Z . From this, we can draw the conclusion that it must be possible to find a correlation function between the R/C and the Z_{eff} . Therefore, knowing the R/C, it is possible to obtain the Z_{eff} of the samples of unknown or partially known compositions (e.g., our vegetable oils); furthermore, it is possible to distinguish them from the X-ray scattering spectra without evaluating the X-ray fluorescence characteristic lines, but by comparing the Z_{eff} and/or the R/C.

2.2. Experimental setup

The confocal EDXRF spectrometer has been described in detail elsewhere (Li, Liu, Sun, Ma, & Ding, 2015). The X-ray source was a Mo rotating anode X-ray generator (RIGAKU RU-200, 60 kV and 200 mA, Rigaku Corporation, Tokyo, Japan) with a spot size of $300 \times 300 \mu\text{m}^2$. For all the measurements performed in this work,

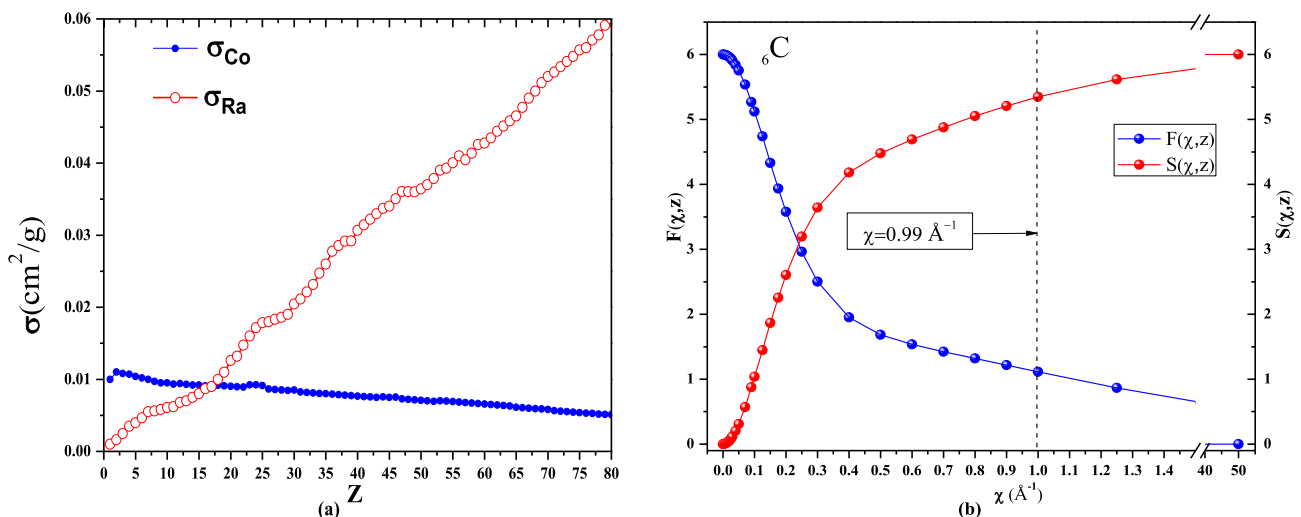


Fig. 1. (a) Z dependence of the Rayleigh and Compton scattering coefficients (data from Hubbell et al., (1975)) for Mo K_α under the scattering angle of 90° . (b) $F(\chi, Z)$, $S(\chi, Z)$ dependence of χ for pure carbon (data from Hubbell et al., (1975)). The vertical dash line marks the momentum transfer χ of $\text{Mo}K_\alpha$ used in this work.

Table 1

Compositions of different vegetable oils (in 100 g of each) based on the values found in their labels, respectively.

Oil type	Total fatty acid (g)	Saturated fatty acid (g)	Monounsaturated fatty acid (g)	Polyunsaturated fatty acids (g)	Trans fatty acid (g)	Carbohydrate (g)	Vitamin E (mg)
Peanut	99.9	17.8	43.9	38.2	0	0	42.06
Soybean	100	15	32	53	0	0	93.08
Sunflower	100	15	32	53	0	0	35
Corn	100	15	32	53	0	0.5	20
Sesame	100	15	40	45	0	0.2	68.53
Mueloliea EVOO	91.6	13.7	68.7	9.2	0	0	–
Betis EVOO	100	14	79	7	0	0	–
Andasaludsia EVOO	99.9	15	79	5.9	0	0	–
Hojiblanca EVOO	100	13	79	8	0	0	–
Agric EVOO	100	14	77	9	0	0	–
Oliviá EVOO	100	15	78	6.5	0.5	0	–
Sceres EVOO	100	15	78	7	0	0	20

the X-ray source was operating at 30 kV and 20 mA. The detector system was an Amptek Si-PIN (Amptek, Inc. U.S.A.) detector. The maximum count rate of the detector system was 2×10^5 counts/s. The energy resolution of the detector system was 145 eV at 5.9 keV. For the purpose of creating a probing volume, the divergent X-ray beam from the X-ray source was focused by the PFXRL and the PPXRL was placed confocally with the PFXRL. Thus, the PPXRL and the PFXRL were aligned to a common point. The confocal technique effectively avoids the scattering contribution from the sample container as the sample was moved to locate at the confocal position and only fluorescence and scattered radiation from this probing volume can be detected (Li et al., 2015).

2.3. Sample preparation

The samples of vegetable oils, including peanut, soybean, sunflower, corn, sesame, and several brands of extra virgin olive oil (EVOO), were purchased from local supermarkets. The compositions of the different vegetable oils based on the values that appear on their respective labels are shown in Table 1.

2.4. Procedure

The polyethylene cells with an external diameter of 32 mm and a capacity of 3 mL of sample, were from Chemplex Industries Inc., reference 1330. The Mylar™ film with a thickness of 2.5 μ m was adapted to the sample cells. One milliliter of each commercial vegetable oil sample was placed in the cell on the Mylar™ film, and was then irradiated for 100 s with the use of confocal EDXRFs spectrometer. All the samples were measured under the same scattering geometry. A Zr filter was employed to obtain the quasi-monochromatic Mo K α line and to reduce the background continuum.

3. Results and discussions

3.1. Function curve of the R/C versus the Z_{eff}

One way to exploit the analytical information carried by the R/C with respect to the Z_{eff} of the investigated samples of unknown or partially known compositions is to construct a calibration curve with materials of well-known elemental compositions. In the “theoretical basis” section, it was stated that for a given momentum transfer χ , the R/C is a complicated function of the Z_{eff} : $R = f_{\chi}(Z_{\text{eff}})$.

To construct the function between the R/C and the Z_{eff} , pure chemical elements (atomic number Z from 1 to 30) were used, as their scatter form factor $F(\chi, Z)$ and incoherent scattering function $S(\chi, Z)$ are already known, and were extracted from the results

obtained by Hubbell et al. (1975). For example, Fig. 1b shows the dependence of $F(\chi, Z)$ and $S(\chi, Z)$ with the χ of pure carbon for the two types of scattering, i.e., both the Rayleigh and Compton scattering. Thus, on the basis of Eq. (12), the R/C was obtained for the pure element. Therefore, the function $R = f_{\chi}(Z_{\text{eff}})$ can be constructed by fitting it with an adequate mathematical function based on the discrete values of $R = f_{\chi}(Z)$ for the pure chemical elements.

Fig. 2 shows the function relationship between the R/C versus the Z_{eff} . The solid curve represents the best-fit polynomial curve (a correlation coefficient r^2 of 0.99997 was found) through points corresponding to the R/C of the pure chemical elements. As expected, the high sensitivity of the curve in the Z_{eff} range below 14 is clearly visible, and will be exploited for identification of different vegetable oils. Nevertheless, this function curve needs to be validated, and this is discussed in the following subsection.

3.2. Validation of the function curve

Table 2 compares the results of the theoretical and experimental values of the reference materials of pure elements, compounds and mixtures with known compositions. The theoretical value of Z_{eff} of a multi-element material can be calculated according to the formula:

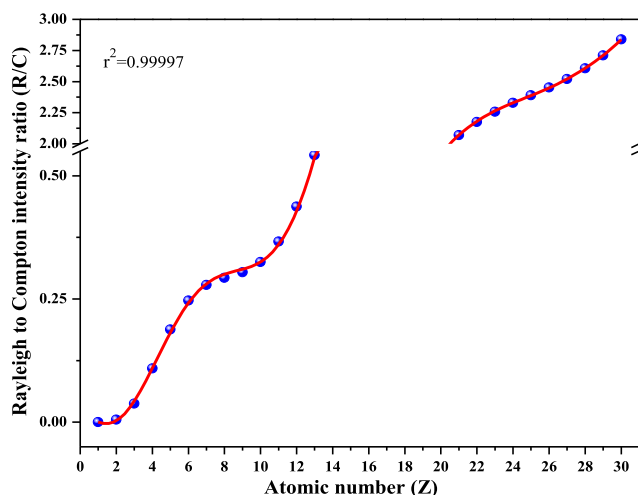


Fig. 2. Plot showing the function relationship between the R/C versus Z_{eff} . Blue symbols represent theoretical R/C values calculated using Eq. (12) for pure chemical elements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Results of materials with known elemental compositions used for R/C measurements.

Reference materials	Sample thickness	Purity (mass%)	Sample preparation	Theoretical Z_{eff}	Theoretical R/C values	Experimental R/C values	Experimental Z_{eff}
B	10 mm	99	Powder	5.000	0.188	0.191 ± 0.003	5.066 ± 0.066
PE(C ₂ H ₄)	10 mm	No certificate	Block	5.281	0.198	0.193 ± 0.005	5.204 ± 0.077
PS(C ₈ H ₈)	10 mm	No certificate	Block	5.613	0.216	0.219 ± 0.003	5.629 ± 0.016
H ₂ O	1 ml	100	Liquid	7.213	0.284	0.288 ± 0.004	7.229 ± 0.016
Glassy carbon (C)	10 mm	No certificate	Block	6.000	0.247	0.253 ± 0.006	6.043 ± 0.043
H ₃ BO ₃	1 ml	No certificate	Liquid	7.133	0.278	0.281 ± 0.003	7.197 ± 0.064
Quartz (SiO ₂)	10 mm	No certificate	Block	10.805	0.343	0.338 ± 0.005	10.764 ± 0.041
PVC (C ₂ H ₃ Cl)	10 mm	No certificate	Block	12.211	0.447	0.441 ± 0.006	12.173 ± 0.038
Al	5 mm	99.9995	Block (polished)	13.000	0.542	0.537 ± 0.005	12.927 ± 0.073
Na ₂ CO ₃	10 mm	No certificate	Powder	9.081	0.314	0.307 ± 0.007	9.011 ± 0.070
CaCO ₃	10 mm	No certificate	Powder	12.525	0.485	0.489 ± 0.004	12.617 ± 0.082
Na ₂ CO ₃ (aq)	1 ml	30	Liquid	7.774	0.297	0.301 ± 0.004	8.031 ± 0.067
CuCl ₂ (aq)	1 ml	10	Liquid	8.644	0.307	0.304 ± 0.008	8.323 ± 0.043
Al ₂ O ₃	5 mm	No certificate	Block (polished)	10.646	0.345	0.349 ± 0.004	10.704 ± 0.058
MgO	10 mm	No certificate	Powder	10.412	0.338	0.335 ± 0.003	10.371 ± 0.042
Si	10 mm	99.995	Block	14.000	0.686	0.681 ± 0.005	13.919 ± 0.081
TiC	2.5 mm	99.5	Disk	18.791	1.705	1.697 ± 0.008	18.695 ± 0.095
VC	2.6 mm	99.5	Disk	19.756	1.897	1.903 ± 0.006	19.815 ± 0.059
Ca	10 mm	99.5	Disk	20.000	1.933	1.937 ± 0.004	20.038 ± 0.038
Cr ₂ N	2.2 mm	99	Disk	20.713	2.036	2.028 ± 0.008	20.653 ± 0.060
Ti	3 mm	99.7	Disk	22.000	2.175	2.171 ± 0.004	21.913 ± 0.087
V	3 mm	99.5	Disk	23.000	2.258	2.251 ± 0.007	22.915 ± 0.085
Cr	13 mm	>99.5	Disk	24.000	2.329	2.323 ± 0.006	23.926 ± 0.074
Fe	3 mm	>99.9	Disk	26.000	2.452	2.447 ± 0.005	26.097 ± 0.097
Cu	3 mm	>99.9	Disk	29.000	2.709	2.714 ± 0.007	29.085 ± 0.085
Zn	3 mm	>99.9	Disk	30.000	2.839	2.843 ± 0.004	30.073 ± 0.073

$$Z_{\text{eff}} = \sum_i a_i^{\text{at}} \cdot Z_i \quad (16)$$

where a_i^{at} is the atomic percentage and Z_i is the atomic number of the element i . As can be seen from Table 2, the experimental values of Z_{eff} are in good agreement with the theoretical values. The relative errors of the experimental values compared with the theoretical values are due to the uncertainties on the evaluations of the peak areas, sample mass thickness, photo-peak efficiency, and statistical error. The inhomogeneities in the sample density and elemental concentration, or excitation of the sample substrate, etc, may possibly increase the estimate uncertainty, for example, our test mixture of aqueous solutions shows relatively large errors. The validity of this function curve, however, is quite satisfactory. As stated previously, when the R/C is obtained, the corresponding Z_{eff} can easily be derived from this calibration curve for any compound or mixture of unknown or partially known compositions that are tested under the same experimental conditions.

3.3. Application of X-ray scattering to the identification of different vegetable oils

The original EDXRF spectra corresponding to different vegetable oils and the expansion regions (between 16 keV and 18 keV) of the X-ray scattering corresponding to $\text{Mo } K_{\alpha}$ line are shown in Fig. 3.

As can be seen from Fig. 3a, X-ray fluorescence peaks of the main light elements C, H and O are not observed due to the poor fluorescence yield, extremely weak excitation, strong absorption in the beam pathway, and overlap with the high spectral bremsstrahlung background in the low energy range. The fluorescence signals of higher-Z elements, like iron, nickel, copper, and zinc in oils, are observed with very low intensity. The determination of high-Z elements in oil samples by confocal EDXRF without pre-concentration was not possible as the technique is not sensitive enough to quantify trace elements. Considering the expansion X-ray scattering region shown in Fig. 3b, a visual identification of

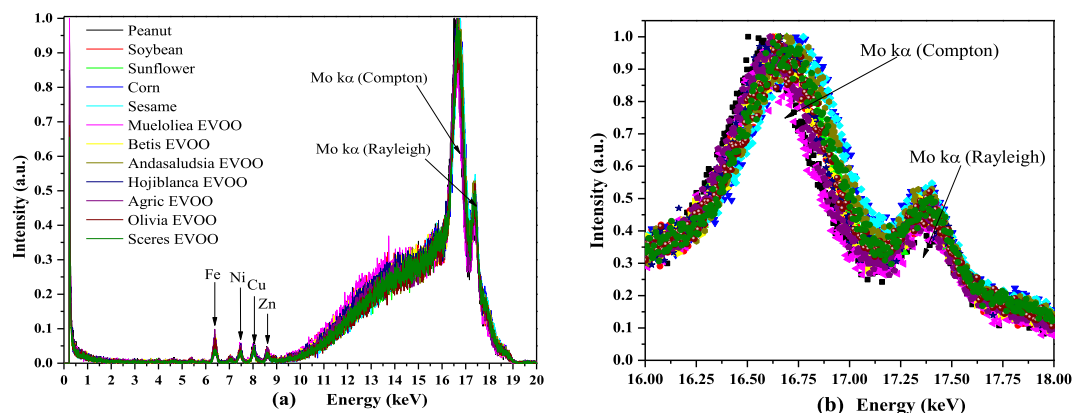


Fig. 3. (a) Original EDXRF spectra corresponding to different vegetable oils, respectively. (b) Expansion of the region of the X-ray scattering used in this work from 16 to 18 keV is shown. The Rayleigh and Compton peak intensities are influenced by the chemical composition of the different oil samples.

the vegetable oils seems impossible due to the peak overlap. In fact, from Table 1, a considerable variation in the chemical composition can be seen, since the lipid acid contents vary over a wide range in the different vegetable oils; these variations in contents produce only small alterations in their spectral profiles, so the apparent scattering from different vegetable oils is still very similar. However, based on extra-high sensitivity R/C approach, it is possible to distinguish the slight differences in their effective atomic numbers. The X-ray scattering spectrum was fitted and the areas under the scatter peaks were evaluated (peak deconvolution and background subtraction) using the QXAS software package from IAEA (International Atomic Energy Agency (IAEA, 1996)). The QXAS fitting procedures allow the spectral evaluation using either Gaussian or Voigt peak profiles. The results of Z_{eff} of different vegetable oils are shown in Table 3. Organic contents have a considerable influence on the X-ray scattering region, thus, X-ray scattering is adequate to analyze organic matrices, at least sufficiently to classify them. When compared with the conventional EDXRF approach combined with principal components analysis (PCA) proposed by Bortoleto et al. (2005), which needs computation of the derived parameters (scores and loadings) for classifying vegetable oils, the advantage of our proposed R/C approach is that we can directly analyze the spectral profiles, as well as avoid the scattering contributions come from sample containers with the confocal technique (Li et al., 2015). This is a powerful use of confocal EDXRF equipment, which was previously considered inadequate for the analysis of materials composed of mainly light elements.

Table 3
Calculated R/C and Z_{eff} with the measurement errors of different vegetable oils.

Oil type	R/C	Z_{eff}
Peanut	0.221 ± 0.005	5.665 ± 0.046
Soybean	0.234 ± 0.004	5.912 ± 0.036
Sunflower	0.225 ± 0.003	5.747 ± 0.013
Corn	0.229 ± 0.005	5.814 ± 0.039
Sesame	0.241 ± 0.002	6.059 ± 0.018
Mueloliea EVOO	0.202 ± 0.003	5.352 ± 0.013
Betis EVOO	0.209 ± 0.004	5.472 ± 0.017
Andasaludsia EVOO	0.216 ± 0.003	5.576 ± 0.026
Hojiblanca EVOO	0.180 ± 0.005	5.012 ± 0.046
Agric EVOO	0.187 ± 0.004	5.104 ± 0.030
Oliviá EVOO	0.205 ± 0.006	5.389 ± 0.055
Sceres EVOO	0.196 ± 0.007	5.244 ± 0.073

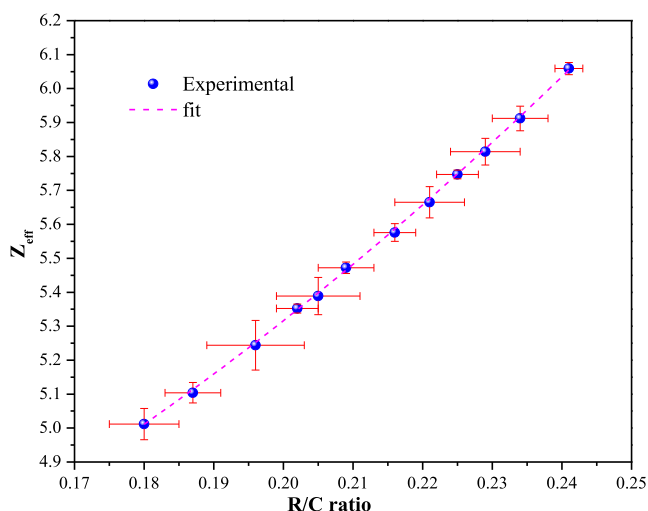


Fig. 4. Experimental results and fitting for the R/C ratio and Z_{eff} of different vegetable oils.

Meanwhile, this proposed alternative method of calculation of the R/C and the Z_{eff} is of practical use for identifying different vegetable oils with high precision and accuracy. Fig. 4 shows the experimental values (Table 3) with error bars of the R/C and the Z_{eff} , and a fitting curve was simultaneously obtained ($r^2 = 0.9995$). As mentioned above, the different vegetable oils are clearly distinguished, and based on the fitting curve, any unknown oil samples or adulteration oils can be identified as their main components are light elements of C, H, and O. The R/C method should not be considered as a completely general method for all analytical problems, it is quite precise and rapid for the many cases in which such a method may be used.

4. Conclusions

The intrinsic property of matter of low atomic number to scattering Rayleigh and Compton X-ray radiation was exploited in this work. Based on the proposed R/C method, vegetable oils with slight differences in Z_{eff} were efficiently discriminated by using a confocal EDXRF spectrometer. This approach is very simple and practical on the basis of a reliable physical model for X-ray scattering, involving only the use of a calibration curve of the R/C versus Z_{eff} , which is constructed by fitting the discrete values of the R/C of pure chemical elements, and has been validated by testing against materials of known compositions. The proposed innovative methodology with the advantages of simplicity, rapid, nondestructive, requires minimal sample handling and data treatment, without generating any kind of chemical residuals, which is a promising alternative to the traditional methods requiring pre-treatment of samples, such as solubilization in solvents, extraction, etc. Also, the methodology is extremely useful and convenient in situations where the main composition is low-Z elements of the analytes, which are not easy to analyze by the conventional EDXRF and/or TXRF techniques. Thus, the R/C approach based on confocal X-ray scattering has potential applications for the routine quality control of vegetable oils, especially for routine analysis in countries where olive oil falsifications with others of inferior quality are frequent.

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