



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 (Strelt 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:

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

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