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Identification of historical polymers using Near-Infrared Spectroscopy

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ABSTRACT

Portability of instrumentation, non-destructive spectral acquisition and a wealth of information that can be extracted from the spectra are features that have made Near-Infrared Spectroscopy an attractive topic in the analysis of cultural heritage.

In this paper, a classification rule was developed using 41 classes of 535 historical and modern polymers using Near-Infrared Spectroscopy. The usability and the quality of the prediction model were tested on a blind sample set of 32 historical polymers. 20 out of 23 samples (87%) which are in the database used for the development of the classification model were correctly classified by the model. Eight darkly coloured samples could not be classified due to their low reflectance. The results of Near-Infrared Spectroscopy are compared to Attenuated Total Reflectance Fourier-Transform Mid-Infrared Spectroscopy and Pyrolysis-Gas Chromatography/Mass Spectrometry. Advantages and limitations of these techniques for the identification of historical polymers are discussed.

1. Introduction

Synthetic and semi-synthetic plastic materials have been used for over a century [1] and today artefacts made from them are an integral part of numerous modern art museum collections worldwide. Unfortunately, many man-made mouldable polymeric materials are relatively short-lived compared to other materials found in historical collections, such as wood, stone, bone, paper and parchment. For instance, poly(vinyl chloride) is a common plastic in museum collections [2] that in a plastic collection survey at the British Museum was found to be most in need of conservation [3]. Characterization of the growing number of plastic materials in museums is, thus, essential for assessing the longevity of the materials, establishing proper storage conditions and informing conservation practice [4]. It also aids in addressing safety issues related to the migration and emissions of plasticizers [5] such as phthalate and bisphenol-A, which are recognized endocrine disruptors [6]. In addition to their adverse health effect, they may be potentially hazardous to nearby artefacts [7–9].

Many techniques are used for identification of plastics. Among the most often used ones are mass spectrometry (MS) [10,11], nuclear magnetic resonance (NMR) [12,13], vibrational spectroscopies such as infrared spectroscopy in mid- and near-infrared region (MIR and NIR) and Raman spectroscopy [14–17], laser-induced breakdown spectroscopy (LIBS) [18–20], thermal analysis [17,21,22] and energy dispersive X-ray fluorescence spectroscopy (EDXRF) [23]. However, despite the availability of numerous techniques, characterization of cultural heritage objects presents many challenges. Ideally, the methods should be non-destructive to the artefact. The instrumentation should be portable, as many objects cannot be transported outside the museum collection for reasons of security or because of size. Additional requirements, such as low cost of the instrumentation and ease of use, facilitate collection surveys and routine analysis of objects prior to conservation treatment.

The majority of the above mentioned techniques (MS, LIBS, NMR) require that samples are removed from the artefact. This is not the case with vibrational spectroscopic techniques. In addition, portable Raman, MIR and NIR spectrometers are available at affordable prices. When combined with spectral databases and a dedicated software these techniques are also user friendly and the results are available in real-time.

Due to these features Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR) in the Mid-Infrared

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(MIR) region has become the most widely-used technique for characterization of historical plastics [24,25]. A significant drawback of the technique is that a pressure is exerted on the sample during collection of the spectrum, which may leave a permanent impression on many pliable plastics, rendering the method unsuitable for the analysis of such artefacts [25]. To the contrary, spectra collection with NIR and Raman may be contactless or require an optical probe, allowing for flexible, mostly non-destructive spectra collection.

In Raman spectroscopy, lasers operating in UV, visible or IR region are used to illuminate the sample and the scattered radiation is collected. Analysis of the spectra enables, with the use of reference spectral libraries, identification of the compounds and reveals some information about chemical structure and physical state of the analyte [26].

NIR spectroscopy relies on absorption of light in the near-infrared region of the electromagnetic spectrum (from about 800 nm to 2500 nm), which induces combination vibrations and overtones of C—H, O—H and N—H chemical moieties in materials. NIR absorption spectra are extremely complex in their nature. Unlike MIR and Raman spectra, NIR bands are typically very broad, consisting of a number of overlapping absorption bands, which often necessitates that statistical methods are used in order to extract information from the spectra [27].

The approach typically relies on a training a classification rule using a large set of calibration samples, whose true class membership is determined using other analytical techniques. Multivariate classification techniques are then used to derive a statistical model that can predict the class membership of new samples based on their NIR spectral data. This process usually requires the pre-processing or normalization of NIR data and the identification of a subset of the NIR variables that are informative for distinguishing the classes. Many multivariate classification methods have been used for classification of NIR data [28]. Discriminant Analysis (DA) is multivariate classification method [29] that finds the linear combination of the variables that best discriminates the groups. Similarly, support vector machines (SVM) [30–32] attempt to find a linear combination of the variables that minimizes the number of misclassifications; the method differ from DA in the way in which the weighting of the variables is obtained.

Classification trees (CART) [33,34] select the variables and their threshold values that split the samples in groups that are most homogeneous in terms of class labels. The process is binary and hierarchical and it is repeated until a termination criteria is met. k-Nearest neighbours methods (k-NN) [35,36] classify a new sample identifying its k nearest units in the training set (neighbours); the class membership of the new sample is defined by majority voting among class memberships of the neighbours. Different distance measurements can be used to find nearest neighbours [37].

Several studies compared different classification methods for NIR data on real data [38–42]. Most frequently, soft independent modelling of class analogy (SIMCA) [38,39,43–45], partial least square discriminant analysis (PLS-DA) [40,41], linear discriminant analysis (LDA) [38,39,41,42], quadratic discriminant analysis (QDA) [38,42], regularized discriminant analysis (RDA) [38], k-nearest neighbours (k-NN) [38,41,42], support vector machines (SVM) [38,41], artificial neural networks (ANN) [38,41,45], support vector data description (SVDD) [41,46], partial least square beta classification (PLSBC) [47] and classification and regression trees CART [48,49] have been applied. From the studies it cannot be concluded which is the overall superior method, as the results depend on the specific data included in a particular study.

NIR spectroscopy has been used for identification of plastics, most notably in relation to recycling [50–52].

Today, commercial databases of NIR spectra are available for various materials, including polymers and additives [53] and specific applications for classification of most common plastics have been developed mainly for the purpose of recycling [54]. Its applicability to the identification of museum artefacts is limited, as the underlying database does not include historical polymers, such as cellulose nitrate, rubbers and formaldehyde-based resins, which in a recent survey together with cellulose acetate contributed to 40% of identified polymers in museums [2]. The survey also showed that rubbers, poly(vinyl chloride), cellulose nitrate and acetate were in a particularly poor condition [2]. Identification of unstable polymers is of particular importance, as it allows timely preservation and conservation actions.

In addition to identifying most of the plastics found in museum collections, a dedicated application for identification of museum objects would benefit also from distinguishing between natural polymers, which may be found in historical collections, such as amber, tortoiseshell, horn and similar and plastics.

The paper presents the results of the development of a targeted application for the identification of polymers in museum collections based on Near-Infrared Spectroscopy and, on a limited set of historical materials, compares it with two other techniques, FTIR and Py-GC/MS.

2. Materials and methods

2.1. Samples used for the development of the classification models

The collection of materials used for calibration of the NIR spectrometer and definition of the classification rules contained 535 samples. It included 87 samples from the “SamCo” reference sample collection of plastic objects, which represents undegraded and degraded materials found in museum collections throughout Europe, comprising the main families of polymers such as polyurethane, poly(methyl methacrylate), cellulose nitrate, cellulose acetate and poly(vinyl chloride). The “SamCo” collection was analyzed by the partners of the 7th Framework Project POPART [55] using a number of different techniques, such as FTIR, Py-GC/MS, Evolved Gas Analysis Mass Spectrometry, Raman, dielectric spectroscopy and differential scanning calorimetry [56]. Additionally, 47 polymers from ResinKit™ (The Plastics Group of America, RI, USA) were used, as well as 401 samples from the collection of Karakta, which came from personal collection of the authors and flea markets and are mostly of unknown manufacturing date. In total, 41 different polymer types were analyzed, as listed in Table 1.

Altogether, the collection of samples represents well the types of materials found in historical collections. When compared to the three recent surveys of historical plastic collections [2], where 89% of plastics were identified, only one plastic (polychloroprene), representing 1% of the historical collections, is not represent in our database. The distribution of plastics in the survey and in our collection is also similar.

2.2. Blind sample set

The 32 samples of the blind sample set (Table 2) were used for comparing the performance of various analytical methodologies. They were not used to validate the NIR classification model, for which the samples and the methodology described in the Section 2.3.1 were used. Blind sample set is not representative of a typical historical collection. In addition to typical polymers found in historical collections, some materials were added as they are challenging for identification. The samples were classified using NIR spectroscopy using the developed classification model. These samples were also analyzed at the Getty Conservation