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Elemental and molecular profiling of licit, illicit, and niche tobacco

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ABSTRACT

The recognition of differences between regulated large-scale mass manufactured products and the uncontrolled cultivation of tobaccos for illicit purposes plays a significant role within identification of provenance. This research highlights X-ray fluorescence and Fourier transform infrared spectroscopy as useful analytical techniques for the rapid identification of tobacco samples of unknown provenance. Identification of key discriminative features within each technique allowed for the development of typical characteristic profiles for each type of tobacco. Analysis using X-ray fluorescence highlights chlorine, potassium, calcium and iron as key elemental indicators of tobacco provenance. Significant levels of chlorine seen within Snüs samples prompted attempts to visualise chlorine containing regions and structures within the sample. Scanning electron microscopy images showed crystalline structures visible within the Snüs tobacco, structures which Energy dispersive X-ray spectroscopy qualitatively confirmed to contain chlorine. Chloride levels within Snüs samples were quantified using ion chromatography with levels found to range between 0.87 mg mL^{-1} and 1.28 mg. Additionally, FTIR indicated that absorbances attributed to carbonyl stretching at 1050–1150 cm^{-1}, alkane bending at 1350–1480 cm^{-1} and amide I stretching at 1600–1700 cm^{-1} highlighting a spectral fingerprint region that allowed for the clear differentiation between different types of tobaccos using PCA analysis, but was limited by differentiation between provenance of cigarettes and hand rolled tobacco. X-ray fluorescence and Fourier transform infrared spectroscopy yielded different information with regards tobacco discrimination and provenance, however both methods overall analysis time and cost reduced indicating usefulness as potential handheld analytical techniques in the field.

1. Introduction

1.1. Licit, illicit, and niche tobacco

Illicit tobacco is typically sold in the form of cigarettes or hand rolled tobacco, which is grouped by U.K. trading standards and Her Majesty's Revenue and Customs (HMRC) into two main groups: counterfeit products, or 'Cheap Whites' [1,2]. Counterfeit tobacco products mimic licit brand packaging in an attempt to masquerade as licit products and contain low-grade unregulated tobacco, which is sold to unsuspecting consumers. In comparison, 'Cheap Whites' are cigarettes that utilize poor filters and low grade tobacco marketed under illicit brand names purely targeted for sale to the U.K. illicit market [1].

Niche tobacco products vary drastically in content depending on the desired method of ingestion, where the product can be consumed without full or any pyrolysis [3]. Niche tobacco is a source of licit tobacco from another country consistently prohibited from sale on the U.K. market. These products do not typically meet standards set out in U.K. or European legislation due to limited knowledge of adverse health effects and contents information [3]. Niche tobacco has over time increased in popularity all over the world, predominantly due to the nature of socialization associated with its use [4,5].

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1.2. Elemental analysis of tobacco

Many of the chemical substances that are associated with the tobacco plant are attributed to atmospheric depositions or the application of phosphate fertilizers and sewage sludge [6,7]. The International Agency for Research on Cancer has highlighted tobacco as a major source of known cancer causing heavy metals with such as cadmium and lead. These heavy metals are found within the body adipose tissues after long term accumulation and are linked to life threatening non-cancerous toxicity of the cardiovascular and renal systems [8]. Tobacco plants are highly susceptible to the accumulation of bioavailable elements such as cadmium (Cd), lead (Pb), and zinc (Zn) through preferential uptake mechanisms whereby the presence of one mobile element within the soil will stimulate the uptake of others [7,9]. Levels of these bioactive elements decrease in the following order throughout the tobacco plant: roots > leaves > fruits > seeds [10]. The interaction of Cd^{2+} and Pb^{2+} with sulphur–hydrogen bonded groups inactivating enzymes to disturb the metabolic process within the cell [7,10]. Unlike organic materials found in soil, inorganic impurities are not usually removed from a source by chemical or microbial degradation [11,12]. Elemental fingerprints are typically detected using inductively coupled plasma mass spectrometry (ICP-MS), however, this technique is not practical for rapid on scene diagnostics that are required by U.K. Trading Standards and HMRC due to time constraints and the need for aggressive digestion methods that destroy evidence vital for criminal convictions [8,13]. X-ray fluorescence (XRF) has previously been scaled down and applied for safe handheld use as an economical and sensitive technique to provide a bulk elemental profiles of plant foliage in under 15 s, easily translatable to tobacco analysis [14–16].

1.3. Spectral analysis and identification of plant material

In some cases, especially to the untrained eye, it is extremely difficult to distinguish visually between licit and counterfeit tobaccos. However, examinations conducted by experienced officers and knowledge of illicit packaging trends at seizure allows for a subjective decision to be made with regards prosecution charges against criminals [17]. A rapid, simple, spectroscopic method of tobacco analysis has the potential to establish a platform for highly discriminative identification of provenance. Due to the complex chemical mixtures found within plant foliage, it is not currently possible to definitively isolate a single absorption band and attribute it to a specific plant constituent, such as chlorophyll, when comparing different types of tobacco [18]. New advances in Fourier transform infrared spectroscopy (FTIR) that have led to improved detection limits and resolution allows for the determination of minor changes in the alkaloid fractions of tobacco, a method which has been adopted by the tobacco quality control industry for the identification of tobacco disease within plants during the incubation period [19].

This research highlights 'user-friendly' rapid methods of tobacco provenance determination in an effort to reduce current costly protocols and potential conflicts of interest with regards current costly outsourced laboratory tobacco analysis using ICP-MS, gas chromatography – mass spectrometry and isotope ratio – mass spectrometry (IR-MS). This research also offers insights into techniques that do not require the destruction of evidential samples by extraction and digestion. By focusing on differentiation between whole spectra, rather than the specific absorbance's of target alkaloids, this research utilizes a simple analytical technique in tandem with multivariate data analysis to highlight tell-tale fingerprint regions that identify tobacco sample provenance.

Table 1
Definition, descriptions, and quantity of different types of tobacco included within this study, all definitions are adapted from the NTPD website [3],http://www.ntpd.org.uk accessed on 08/11/2015 at 23.07.

Tobacco	Definition and description	Number of tobacco samples within study
Cigarettes	Cigarettes are the most common tobacco product available on the market, made up of flakes of tobacco leaf that have been rolled into a cylindrical shape using a filter and thin filter paper	45
Miniature cigars	Miniature cigars are roughly the same size as a cigarette, made using large tobacco flakes rolled in whole tobacco leaf to allowing for a slower rate of pyrolysis	2
Hand rolled	Hand rolled tobacco is usually a blend of several types of tobacco, with thin wiry strands that are rolled using filter paper into a cigarette form or alternatively smoked in a pipe	16
Khaini	Khaini has a predominantly male market within India and Pakistan. Consumed socially, the user combines the Khaini by pressing it into the form of a ball, then places it in the oral cavity where it is then held and sucked occasionally for 10–15 min. Khaini contains fragments of leaf material, tobacco, slaked limed paste and areca nut	2
Gutkha	India and Pakistan are the main retailers and consumers of Gutkha products, with a target market of young men and boys. Gutkha is sucked, spat or chewed and typically contains betel nut, catechu, tobacco, lime, saffron and additional flavouring agents specific to the brand	4
Snuff	Fire cured tobacco, more commonly known as snuff, is found in a dry powdered form with less than 10% moisture content which is then either sniffed or held in the oral cavity. Snuff is a product typically found within the U.K, USA, India and Sweden	2
Snüs	Predominantly produced in Sweden on a large scale, Snüs is found in either loose or pouched form with a typical portion being between 0.5 g and 1.0 g. The pouch or loose tobacco is held in between the wet membrane of the gum and cheek to allow for rapid absorption of constituents into the blood stream. The tobacco is finely ground, dried and mixed with aromatic substances, salts, humidifying agents such as Sodium Carbonate, additional nicotine and water	5
Shisha	Shisha or water pipe tobacco, the composition of which varies and is typically found to have thick almost bark like fragments of tobacco leaf mixed with artificial flavourings. Additional nicotine and aromatic compounds are present resulting in a sticky oily residue that is used to give a specific desired fragrance to the tobacco. Shisha tobacco is marketed based on flavour/fragrance and is typically produced in North African countries, Eastern Europe and Southern Asia	3