Detecting Counterfeit Beverages using Analytical Techniques related to HPLC/GC/CE

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Abstract: Fraud in beverages is now more common due to the continuous growth in the beverage industrial sector globally. Therefore, there is a need to continually monitor beverages flooding the markets for counterfeits and quality assurance purposes. This report presents a review of recent techniques employed in the detection of counterfeit or fraudulent beverages. Particular focus is given to techniques found to be related, hybridised or within the bigger technique-groupings of High-performance liquid chromatography (HPLC), Gas chromatography (GC) and Capillary electrophoresis (CE). The advantages and limitations of the techniques are discussed, while highlighting alternative methods, technological advancements and future potential.

Keywords: High-performance liquid chromatography (HPLC), Gas chromatography(GC), Capillary electrophoresis (CE), Miscellaneous techniques, Food, Beverage, Quality Assurance

1. INTRODUCTION

All over the world the beverage industry is a continuously growing sector. The global beverage industry is supposed to touch the mark of $1.9 trillion by 2020 (Amit and Sirshendu, 2019). Due to high demand of some beverages and food, a lot of fraud has been identified in beverages. The adulterants in beverages can be classified as targeted, non-targeted and economical motivated according to Jeffrey; Pfeifer; Kendra; Majors and Ronald (2014), which maintained that the use of some non-chromatography techniques such as Mid – Infrared (MIR) and near Infrared(NIR) has yielded a good result in the detection of counterfeits beverage. Also High-performance liquid chromatography (HPLC) combined with variety of detection methods ranging from ultra-violet (UV) to mass spectrometry has also be proven to be a good technique in the detection of false product. Therefore, this report presents a review of recent techniques employed in the detection of counterfeit or fraudulent beverages. The advantages and limitations of the techniques are discussed, while highlighting alternative methods, technological advancements and future potential. Particular focus is given to techniques found to be related, hybridised or within the bigger technique-groupings of HPLC, GC and CE.

2. DETECTING THE LEVEL OF CAFFEINE IN BEVERAGE PRODUCTS

Caffeine (1, 3, 5-trimethylxanthine) which belong to a group of methylxantines, has its minor isomeric dimethylxanthines being theobromine and theophylline (Komes et al., 2009), while Akyilmaz & Turemis (2010) highlighted that this group to which caffeine is member, methylxanthines, could be present in many painkillers and antimigraine pharmaceuticals.

Figure 1. Chemical Structure of Caffeine (Source: Ali et. al., 2012)
Detecting Counterfeit Beverages using Analytical Techniques related to HPLC/GC/CE

The Figure 1 shows the chemical structure of caffeine. Caffeine is beneficial in the improvement of cardiac performance but could be dangerous when found in urine at the concentration level of 12 µg/mL which has adverse effect (Ali et al., 2012). The study further stressed that any beverage having caffeine in excess of about 150 µg/mL must have it indicated on the label, while stating that to determine some artificial or counterfeit sweetener such as saccharin in some caffeinated beverages, HPLC methods offer developed traceability and accuracy, and also other analytical techniques such as Titrimetric, Spectrophotometry, NIR spectroscopy and capillary electrophoresis are useful in detecting counterfeits. Chou and Bell (2007) suggested coupling Reversed Phase Liquid Chromatography method alongside HPLC-grade, and Komes et al., (2009) used distilled water in preparation of the sample solution and carried out a research in the analysis of caffeine content in five beverages namely coke cola; Pepsi cola; Red bull; Gazaitain Black tea and coffee and the results in Table 1 were obtained.

| Table1. Recoveries of caffeine spiked beverages sample |
|-----------------------------------------------------|
| Amount of caffeine in sample (ppm) | Amount of caffeine added (ppm) | Amount of caffeine found (ppm) | Recovery percentage (%) |
| Pepsi cola | 18.68±0.40 | 20 | 38.47±0.80 | 99.0 |
| Coca cola | 18.29±0.48 | 20 | 39.30±2 | 106 |
| Red bull | 52.62±0.65 | 20 | 72.46±0.35 | 99.2 |
| Gazaltain black tea | 47.29±0.26 | 20 | 67.70±1.50 | 102 |
| coffee | 25.24±1.60 | 20 | 45.64±0.40 | 102 |

a. average ± standard deviation (n=3). Source: Ali et al. (2012)

The study procedure in Table 1 reports that caffeine injection was done by adding 20 ppm to the sample beverage, and from results in the table, it could be observed that RED BULL has the highest level of caffeine concentration. Also, Samples of black tea samples, energy drink was taken by Ali et al 2012 to detect the level of caffeine and the following chromatography was obtained.

![Figure 2. Energy drink Chromatograph (Ali et al., 2012)](source)

The chromatograph of energy drink is displayed in Figure 2.

![Figure 3. Black Tea Chromatograph (Source: Ali et al., 2012)](source)
The chromatograph of black tea is presented in Figure 3. An interesting observation from the display is the indication that the black tea sample has the highest caffeine concentration of 440ppm to 473 ppm, with an average value of 458.6ppm. Violeta, Trandafir, and Elena (2008) supported the use of reversed phase liquid chromatography in the separation analysis of caffeine. In its approach, the study used HPLC methods to provide stable retention time alongside with thermo electron system and assay detector, and approach was found to be good for the quantification of caffeine in beverages because it is reproducible, sensitive, precise and also in providing better results. However, Akyılmaz and Turemis (2010), mentioned that the use of HPLC has disadvantages because operator attention is much required in the application and suggested that NIR reflectance spectrometry and FT Infrared are versatile for determination of caffeine content because they do not consume much chemicals.

2.1 Analytical Detection of Fraudulent Coffee

Coffee have two main varieties, namely Arabica and Robusta (Ebrahimi-Najafabadi et al., 2012) and Arabica coffee contain some organoleptic feature which make it costlier. The authors maintained that principal counterfeit of coffee involve roasted and unroasted coffee husk, twigs, barely, chicory, malt, starch, corn maltodexine, glucose sirups and caramelized sugar. UV-vis spectroscopy and HPLC analytical techniques were used by (Hečimović, Belščak-Cvitanović, Horžić, & Komes, 2011) to decide the polyphenols compounds and the content of caffeine is some coffee samples. In support of this research, Ebrahimi-Najafabadi et al. (2012) discussed that Principal Component Analysis (PCA) and Linear Discriminant analysis (LDA) were useful as pattern recognition tools of triglyceride and tocopherol content of roasted and green coffees, which distinguishes tastes between Arabica and Robusta varieties, while (Brondi, Torres, Garcia, & Trevisan, 2016) observed that FTIR coupled with (PAC) is capable to distinguish counterfeit from original sample of coffee by corn at level below 1%. This research maintained that Near Infrared spectroscopy (NIR) coupled with multivariate calibration was also used to measure the amount of coffee huk, corn in Coffee Arabica and to quantify the content of variety of Robusta coffee mixtures (Ebrahimi-Najafabadi et al., 2012).

On the other hand, Jham, Winkler, Berhow, & Vaughn, (2007) highlighted that tocopherol determination was developed in order to detect adulterated coffee by corn using HPLC and therefore Tocopherol fingerprinting gives the potential to detect counterfeit. However, (Oliveira, Oliveira, Franca, & Augusti, 2009) accomplished the separation of the counterfeit and non-counterfeit of coffee with a methodology based on a GC- MS of samples of ground roasted coffee and barley using Solid Phase Micro Extraction (SPME), and chemometric method, which is Principal Component Analysis (PCA) was used to chromatograph the data obtained. “It was observed that, the higher the degree of roast, the more easily discriminated the adulterated samples were, allowing for detection of adulterations with as low as 1% (w/w) roasted barley in dark roasted coffee sample”.

Figure 4a shows a PCA score scatter plot of normalized chromatographic SPME areas of pure coffee and submitted to roasting at 300 °C (pc 1 vs pc 2), where C represents coffee, B represents barely, L= light roast, M = medium roast and D= dark roast (Ebrahim-Najafabadi et al., 2012). Figure 4a shows that despite the volatile profile of roasted coffee in contrast to roasted barley, a perfect separation between roasted coffee and roasted barley was achieved correspondingly. Hence multivariate of
statistical analysis (PCA) of different compounds was performed to verify the prospect of discrimination at a roasting of 300°C, while the first principal component explained 93.8% and 2.4% of the chromatographic variance. On the other hand, Figure 4b shows the weight lost during roasting that both coffee and barley have same qualitative behaviour as categorized by a slower rate at the onset of roasting as indicated by the tick lines which represent linear fit. Thereby the two straight line represents the two rates.

It could be stated therefore that the detection of counterfeit coffee can easily be made using SPME coupled with Gas Chromatography which is simple, requiring less solvent, although (Ebrahimi-Najafabadi, 2012) argued that chemometrics application of Near Infrared spectroscopy (NIR) is faster, reliable and affordable for the detection of counterfeit coffee. This view was in accordance to what have been suggested in previous reports (Ribeiro et. al., 2011; Enyoh et. al., 2019; Verla et. al., 2019; 2019a).

3. IDENTIFICATION OF COUNTERFEIT WHISKY

Whisky can be generally characterised by three properties, namely: the ethanol content, the congener profile and the colour consistency (McIntyre, Bilyk, Nordon, Colquhoun, & Littlejohn, 2011), hence important in detecting counterfeit products. For example, the study highlights that a Scotch whisky must adhere to a legal minimum content of 40% (v/v) ethanol, containing a range of congeners formed during the fermentation and maturation processes and having a specified colour consistency.

Congeners analysis and various types of HPLC techniques can be combined in beverage content profiling. To detect counterfeit whisky, McIntyre et al. (2011) used two techniques, namely Attenuated Total Reflectance (ATR), which allows in the determination of ethanol concentration with Diamond-tipped immersion probe for Mid-Infrared (IR), and Principal Component Analysis (PCA) used to verify colorant added in dried residue of whisky sample in combination with polycrystalline silver halide optical fibres. The study emphasises that one sided t-test was used to assess ethanol concentration in which some of the samples had a low legal minimum of 40% (v/v), signifying that they are potentially counterfeit.

According to Cantarelli et. al., (2014), PCA technique assist in the decomposition of compounds and can be used in determining the taste and colour of whisky, however Aylott and MacKenzie, (2010) gave a view that due to longer time and specimen used in laboratory, a portable instrument similar to UV-visible spectrometry could rather be used to detect counterfeit whisky. Although UV-visible spectrometry saves time, it also suffers a limitation in providing more comprehensive spectral information unlike the MIR (McIntyre et al. 2011).

For detection of counterfeit whisky, SPME/HRGC/MS were basis for sample preparation and GC/MS and HPLC were used to authenticate and determine counterfeits (Wiśniewska, Dymerski, Wardencki, & Namieśnik, 2014). As observed in this study, it is important to highlight that SPME can be coupled with GC/AED in order to achieve a good result for whisky authenticity. This further implies that to continue developing methods for counterfeit beverage detection, innovation in preparation of samples coupled with right separation techniques is important in producing better spectra. As held by (Castro, Natera, Durán, & García-Barroso, 2008) SPME can work effectively with gas chromatography (GC) and GC-mass spectrometry (GC-MS) and with HPLC; hence removing the need for organic solvent, which is an added advantage.

According to Ashok, Praveen, & Dholakia, (2011), counterfeit whisky can be detected in relation to age, taste and barrels in which they had been aged, on the basis that whisky contains compounds like aldehydes, esters which are also known as congeners that assist in identification of brand and quality of whisky to avoid counterfeit using a chemometric analysis with Near – Infrared Spectroscopy (NIR). However, Wiśniewska et al., (2014) maintained that samples can be analysed using PCA and PLS regression, as counterfeits of scotch whisky can be detected using Mid Infrared spectroscopy technique. This study further shows that some samples of whisky examined have low legal minimum of ethanol content below 40% which makes the Scotch whisky falsified.
Detecting Counterfeit Beverages using Analytical Techniques related to HPLC/GC/CE

The prediction ethanol concentration in various brands of whisky is presented in Figure 5, using the PLS model (Figure 6). By this observation, it could be interpreted that the PLS model works perfectly well in predicting ethanol concentration in whisky samples and hence, it is one of the parameters in the valuation of the quality of whisky to decide the ethanol concentration. Therefore, it can be inferred in this study that calibrated technique (PLS) could be used in fast detection of counterfeit whisky as ethanol concentration must be 40% which is the legal value to show that it is authentic. The figure 5 also showed that the manufacturers specified concentration vary from the predicted ethanol concentrations.

4. TECHNOLOGICAL ADVANCEMENTS IN DETECTION OF COUNTERFEIT BEVERAGES

Many decades ago, detection of counterfeit beverage products has always been done by using physical method or visual inspection, and as reiterated by Ebrahimi-Najafabadi et al. (2012), these methods of detection are inappropriate to distinguish between a genuine product and a fake, whereas UV–vis spectroscopy and HPLC coupled techniques have been employed in recent years, proving to be better than the methods applied in early times. While observing that traditional analytical methods which sometimes could be laboratory-based consumes both time and money, Zhang, Chu et al. (2016) suggested that spectroscopy techniques that are faster, reliable and feasible should be adopted. This study stressed that Near-Infrared spectroscopy (NIR) and Mid-infrared spectroscopy (MIR) are more reliable because of their efficiency in several detections of counterfeit product samples, and Nádia Reis et al. (2013) agreed that spectroscopic methods have proven to be successful in the detection of beverage adulteration.

Traditional methods based on wet chemistry, such as iodine value and saponification value, were used in the last decades for food and beverage authentication as cited by Cubero-Leon (2014), although the traditional method are applicable in product standardisation. Furthermore, the author maintained that Metabolomics, which is a new methodology that can help to deal with the challenge of counterfeit and authentication of beverages and food, where classical methods fail to detect them, highlighting that...
metabolomics application uses of a characteristic untargeted procedure to facilitate the detection of fraud and counterfeit. Metabolomics is centrally suited to identify and quantify a wide array of small molecules which consist of primary and secondary metabolites (Wolfender et al. 2013). Hec’ımovic (2011) suggested that visual inspection, which is one of the ways of detecting counterfeits in old chemistry, should not be jettisoned as this can aid checking the externals of some samples, as applicable in the inspection of external colour of beans as done the coffee roasting industry. Therefore, it could be suggested that both wet and classical chemistry can work hand in glove in detection of counterfeit beverages and food in general.

5. LIMITATION IN COUNTERFEIT TECHNIQUES AND FUTURE POTENTIALS

Solid-phase microextraction (SPME) was used by Oliveira et al. (2009) to detect counterfeit coffee with GC-MS technique, while Cubero-Leon (2014) argued that although SPME has its advantages, it mostly concentrates on volatile compounds. While SPE can be fully automated, another of its limitations as stated by Tredoux et al. (2008) is that it does not provide high sensitivity because of larger sorbent phase volume and therefore an alternative technique known as Stir Bar Sportive Extraction (SBSE), was suggested because it’s provision of more sensitivity. Cubero-Leon (2014) however maintained that despite SPME limitations, Stir Bar Sorptive Extraction (SBSE) cannot be fully automated and does not give the opportunity of choosing a stationary phase, based on the chemical properties of the analyte of interest.

In search for alternatives to SBSE, Tananaki et al. (2007) used another technique known as Purge and Trap (PT) to extract volatile compounds in honey. However, PT technique is not commercially available and also has a low sensitivity range in addition to taking a longer duration during extraction (Cubero-Leon, 2014). Therefore, it important to highlight the necessity that analysts understand the nature of the compounds of interest, and choose better techniques for both extraction and analysis, that are convenient, time saving and able to provide good spectra. However, if a particular research is not only on volatile compounds for example, then the proposed analytical platform will be Gas Chromatography, hence an understanding of the derivation processes will be needed to extract the analyte of interest.

Another research by Tarantilis (2008) used a technique known as Solid Phase Extraction (SPE) to extract wine for analysis, illustrating that wine from grape varieties can be distinguished from counterfeits. This technique is also fast and simple where methanol containing 0.01% hydrochloric acid was used to elute the analyte of interest at stationary phase, but its limitation is that only precise compounds are recovered and the procedure can be lengthy (Cubero-Leon 2014).

Another research carried out by Ali et al. (2012) used NIR technique to authenticate caffeine concentration. In food processing and analysis, NIR technique has 40 years of proven record in the areas of continuous monitoring and quality control, while providing benefits in the form of robustness, instrumentation simplicity, efficiency, precision and portability (Ellis et al., 2012). In Comparison, the study highlights that both NIR and MS techniques, have advantages such as high signal-to-noise ratio, able to simultaneously measure multiple components in samples, and remote sampling capability which allows for the collection of real-time information in a process stream. On further examination, the authors reveal that NIR has two main advantages over IR, namely: having near-infrared light that penetrates much deeper into an intact food sample (>10 mm), as well as through various packaging materials, and the other, being that water absorbance in NIR is not as strong as in MIR, thereby enhancing more routine analyses, with no need for additional accessories. Despite these advantages, it was acknowledged that NIR technique has limitations, with low sensitivity to some minor constituents in samples being a key downside, especially in some complex chemical species.

Furthermore, in counterfeit beverages detection, Remedios et al. (2008) coupled SPME with GC-MS, and (Cubero-Leon 2014) stated that GC separates the component of a mixture, while MS categorises separated components. The study shows that the analyte must be thermally stable and volatile, although GC-MS have high separation power and re-productivity but limitations include being expensive and time consuming. Suggested alternative techniques include Proton Transfer Reaction MS (PTR-MS) and Direct infusion/injection or Analysis in real time (DART)MS, given that these techniques save a lot of time in analysis, and also used to characterise volatile compounds and sample preparation is not needed, for example in SPME with GC-MS (Araghipour et al., 2007).

As the dealers of counterfeit products continue to manoeuvre their ways, improvements in analytical methods to detect counterfeits will continue. Hence, a method known as electron Nose (Chen, Zhao,
& Vittayapadung, 2008), which uses sensors that mimic human olfactory based on cross–reactive sensors has been developed, and another is the Electronic Tongue (Kovács et al., 2010), providing a main feature for the application of non-chemical sensor. These two techniques have the capacity to produce suitable pattern recognition, however their major limitation is the inability to recognise more samples.

6. CONCLUSION

In this review, it has been observed that there is need for more sophisticated techniques in the detection of counterfeit beverages in order to beat counterfeiters. Various techniques and hybrid-techniques within or relations to HPLC, GC-MS, UV–visible spectrometry NIR, mid IR, and some sample-preparation techniques such as SPME, SBSE have been shown to yield good results in the analysis of beverage constituents and detection of counterfeit.

However, considering technological advances, Electron Nose, Electronic Tongue, and Purge and Trap (PT) will be of greater use when made commercially available at affordable rates, and will provide industry players better opportunities to set up their quality assurance laboratories for the detection of fakes and counterfeit products in the market.

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