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Using low frequency full bottle diamagnetic screening to study collectible wine

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ABSTRACT

A low frequency $\nu < 30$ MHz spectrometer capable of noninvasively and nondestructively screening the diamagnetic properties of full intact bottles of wine is described, and along with principal component analysis, used to compare and contrast sealed bottles of wine. The sensitivity of this approach to various ionic and molecular wine solutes is established by analyzing standard solutions. The successful application of this full bottle method to a library of collectible wine is discussed and suggests that the method can be used to identify counterfeit wine without violating the bottle.

1. Introduction

Given that the value of collectible wine can easily approach several thousands of dollars (e.g. the 1985 Petrus Pomerol and the 1982 Chateau Latour are currently valued at $3500 and $2000 respectively [1]) and that high end wines are routinely counterfeited, it is interesting that the wine market has not demanded a method to verify wine authenticity without opening the bottle or violating the bottle seal. A bottle of wine is merely an opaque, often green, glass container housing a dark purple colored liquid that is labeled with a piece of paper having the wine maker mark; this is an easy target for counterfeiters. Whether an authentic empty bottle is backfilled with a lesser quality wine and carefully resealed or a lower grade sealed wine bottle is intentionally labeled with the mark of a higher quality wine, it is the ease of wine modifications and the absence of any available thwarting technology combined with the potentially large financial benefit that makes the selling of faux wines an attractive venture. The wine industry has attempted to stop counterfeiting by introducing high tech cosmetic changes to labels and corks [2–5]. Not only are these counter measures easily defeated, they do not address the fact that older bottles do not have these upgrades and that older bottles currently dominate the wine collection market. Unfortunately these efforts to defeat wine counterfeiters only increase the difficulty associated with marketing counterfeit wine as there is always a way to make an item appear externally authentic. A better approach is to compare the contents of the sealed suspected counterfeit wine bottle to the contents of accepted authentic sealed wine bottles of the same vintage and type. It is the unique flavor, texture, and aroma of wine produced by the specific combination of the numerous chemical constituents that not only makes consumption delightful but also indicates authenticity.

It is the complex wine making process that is responsible for every wine having specific chemical, element, or compound concentrations. The concentration variation of these compounds in wine is due to the viticultural and enological history of the wine or equivalently the details relating to grape growth, harvesting, storage, must extraction, fermentation, and bottling.

The viticultural based chemical compound concentration variability in wine is produced by both natural processes and external sources. Region specific soil conditions [6], the composition of available vineyard irrigation sources [7,8], and the climate [9] contribute to the various salt and ion concentrations in wine as both the quality and quantity of the harvest directly depend on how the grapes are grown. The sugar levels in mature grapes established during the growth process ultimately dictates the concentration of ethyl alcohol [10], glycerol [11], lactic acid [12], etc. following fermentation. These naturally induced chemical compound concentration variations in wine are further augmented by external mechanisms as well. Here environmental pollutants like lead or cadmium [13] can enter the plant if the vineyard is located near an urban environment or a major transportation corridor while sodium ion levels are known to be elevated in grapes obtained from vineyards exposed to ocean spray [14]. The application of fertilizers and pesticides to growing vines also modifies inorganic ion concentrations in wine. Fertilizers directly contribute to varying potassium, calcium, and phosphate concentrations [15] in wine

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while pesticides can introduce cadmium, copper, manganese, lead, and zinc ions [16].

Inorganic and organic based chemical constituent concentrations in wine are also strongly affected by the enological processes applied following the grape harvest. It is well known that storage vessels, piping systems, and transfer containers increase aluminum, cadmium, chromium, copper, iron, and zinc ion concentrations [17]. Flocculants are often added to wine to improve clarity and remove particulate debris. This process further increases the sodium, calcium, or aluminum ion content in wine [18]. The application of pH buffering agents to stabilize wine acidity can add calcium or sodium carbonates to wine while preservation agents like sulfites are introduced to extend the wine lifetime [19]. The concentration of organic chemical compounds in wine is largely controlled by fermentation. For example, the length of the alcoholic fermentation period coupled with the type of yeast used and the naturally occurring grape sugar concentration dictates how much sugar is converted into alcohol [20]. In addition, glycerol formed during alcoholic fermentation may be subsidized with additional glycerol to control viscosity and perceived sweetness [11]. In a similar way the length of the malolactic fermentation period controls the percent conversion of malic acid to lactic acid [12]. Solid sedimentation on the bottom of stored wine bottles is another way that constituent levels may change. Interestingly the formation of bitartarate particulates in standing wine is acceptable to European standards yet it is considered objectionable by most Americans. Thus American wines are typically cold stabilized to crystallize and remove potassium bitartarate prior to bottling thus changing the bitartarate and potassium concentrations in wine [21].

At a concentration of 0.1–3 g/L potassium is the most prevalent ion in wine followed by sodium, calcium and magnesium [22]. It is variations in this high potassium concentration that are governed by soil conditions as mentioned above and the pronounced uptake of potassium by grape vines [23] that makes potassium an excellent geogenic marker. Although the concentration of the paramagnetic ions such as iron, copper, and manganese are substantially lower in wine (mg/L), these ions catalyze oxidative reactions that produce aldehydes, ketones, and carboxylic acids [24]. Thus while the concentration of catalytic amounts of these ions may not be directly quantifiable in sealed intact wine bottles, their effect on the concentration of other wine constituents may be determined.

There are numerous variables that impact the concentration of the inorganic and organic molecular constituents in bottled wine that reflect the viticultural and enological history of the final prepared wine. It is therefore unlikely that any two bottles produced from two different viticultural or enological processes would ever have the same chemical constituent concentrations or ionic and molecular fingerprint. Modern analytical chemistry approaches such as nuclear magnetic resonance (NMR) spectroscopy [25], gas chromatography/mass spectrometry (GC/MS) [26], light absorption [27], scattering [28], and elemental analysis [29] have been used to fingerprint wine. Here it has been shown that amino acid ratios [30], rare element abundance [31,32], or even deuterium quantification [33] afford region specific identification. However, as all of these approaches are invasive or destructive they are not directly applicable to valuable collectible wine. Collectors spending thousands of dollars for a single bottle realize that either opening the bottle or extracting small volumes of wine from the bottle immediately devalue the investment. It is for this reason that noninvasive wine constituent analysis was recently developed. Here high resolution NMR spectroscopy [25,34] and GC/MS [26] applied to full intact wine bottles was used to noninvasively and nondestructively screen bottled wine for oxidative spoilage mediated by leaky corks and for the presence of 2,4,6-trichloroanisole (TCA) or cork taint respectively. Although the NMR approach can monitor down to 100 mg/L acetic acid or acetaldehyde concentrations in wine, the use of full bottle NMR spectroscopy to screen for the lower concentration solutes that reflect wine origin and thus authenticity mentioned above is problematic due to sensitivity and resolution limitations. Here many of the ionic solutes contain non-NMR active or low natural abundance, low gyromagnetic ratio nuclei or are present at concentrations below the NMR detection threshold. The NMR spectra for the higher concentration molecular compounds such as ethyl alcohol, acetic acid, succinic acid, proline, and borate esters often spectrally overlap making identification difficult if not impossible in full intact wine bottles. The much higher sensitivity of the full bottle GC/MS approach is more attractive than NMR spectroscopy but the success enjoyed in the screening of bottle mounted corks for TCA does not apply to fingerprinting as just the outer surface of the cork is examined with this approach not the wine bottle contents.

More recently, low frequency radio waves were used to explore the dielectric response of intact wine bottles [35]. That approach used principal component analysis (PCA) to reduce the collected data into two wine specific data points, and the method described here uses the same basic strategy. Here the frequency dependent magnetic properties of wine in sealed intact bottles are probed by monitoring the effect of the frequency dependent magnetic susceptibility on the amplitude and phase of an applied oscillating magnetic field. The method combines the simple apparatus shown in Fig. 1 and the spectrometer shown in Fig. 2 with PCA [36] to

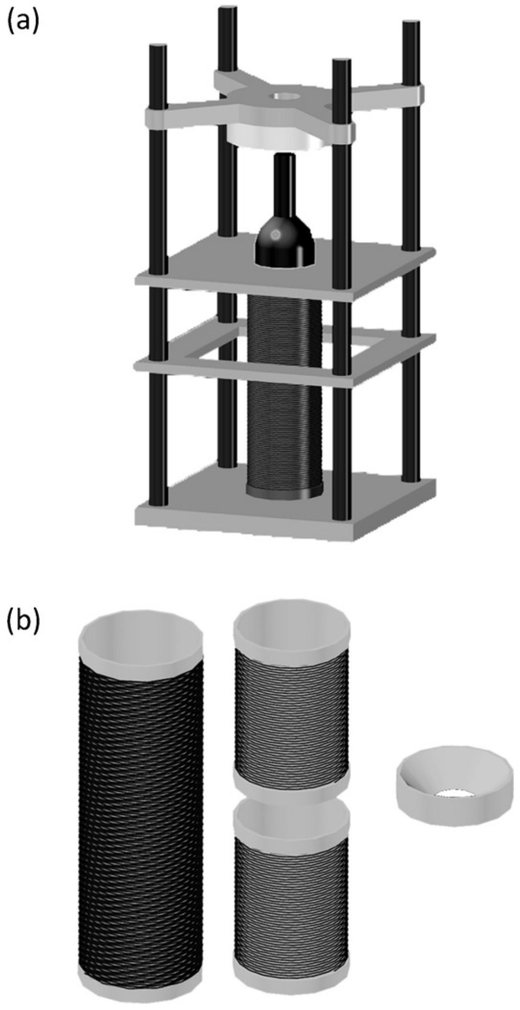

Fig. 1. Rendered image of the device used to monitor the induced magnetization of full intact wine bottles (a) and a separated view (b) showing the secondary coils along with the bottle holding insert.