A global survey of the stable isotope and chemical compositions of bottled and canned beers as a guide to authenticity

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ABSTRACT

This study presents a dataset, derived from the analysis of 162 bottled and canned beers from around the globe, which may be used for comparison with suspected counterfeit or substitute products. The data comprise δ^2H and $\delta^{18}O$ compositions of the whole beer and $\delta^{13}C$ compositions of the dry residue (mostly sugar) together with the concentrations of five anions (F, Cl, NO_3, SO_4, PO_4) and seven cations (Ca, K, Mg, SiO_2, V, Mn, Sr).

A strong correlation, consistent with natural waters but offset from the Global Meteoric Water Line, was observed between the $\delta^2H/\delta^{18}O$ composition of the beers. The extent of the offset could be explained by the brewing process and the alcohol and sugars present in the beers. Correlations between inorganic analytes were consistent with the addition of salts in the brewing process.

Beers were classified as follows: ale, lager, stout or wheat-beer and the chemical composition was found to be characteristic of the assigned type, with lagers being the most readily classified. A combination of chemical and isotopic data was found to be characteristic of the geographical origin (on a continental scale) and could most easily identify beers from Australasia or Europe. A global map of $\delta^{18}O$ data revealed a geo-spatial distribution that mirrored existing maps of the isotopic composition of annual precipitation. This confirmed a commonsense view that local precipitation will be the primary source for the water used in brewing. Using this *isoscape* (or *alcoscape*) it may be possible to assess the geographical origins of samples for which genuine comparative samples cannot be obtained.

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1. Introduction

The authors present results from a survey which assessed the isotopic and chemical (cation and anion) compositions of bottled and canned beers as a means of determining geographical origin and authenticity.

Producers of many different foods are increasingly protective of the cachet which the country, or region, of origin bestows on their produce. In turn, consumers will pay a premium price for what they perceive to be a superior product, attributed to a country or region of renown. The elevated prices associated with such products will, inevitably, lead unscrupulous traders to offer cheaper, inferior goods for sale; presented as authentic products to the detriment of both producer and consumer. This practice also degrades the brand reputation of the genuine product, as counterfeit or substitute goods are unlikely to be of the substance or quality demanded by the consumer. In Australia, for example, many popular European beers are brewed under licence by large commercial operations, with packaging which closely resembles the original product. These products are significantly cheaper than the equivalent imported product and might well be purchased in the mistaken belief that they have been imported.

As a means of protecting both sellers and consumers, food analysts are increasingly looking at stable isotope analysis, often allied with chemical profiling, as a means of determining geographical origin and distinguishing between genuine and counterfeit goods [1,2]. Numerous studies have described the authentication of wine through chemical analysis, especially elemental composition [3–7]. Many studies have also determined the stable isotopic composition of the light and/or heavy elements present in wine [8–10], its ethanol content [11,12] and even the carbon dioxide present in the bubbles of sparkling wines [13,14]. These studies have also demonstrated correlations between isotopic composition and both climatic data and viticulture practices [15], although typically over small geographical regions. The focus on wine comes despite beer having the largest share of the global alcoholic beverage market with total revenues greater than $ 500,000 m in 2012 [16].

In comparison with wine, only a limited number of studies have examined the isotopic and chemical compositions of beers and have primarily attempted to discriminate between styles of beer [17,18]. One study has suggested that a combination of iron, phosphorus, polyphenol and potassium concentrations could distinguish beers from Germany, Portugal and Spain [19]. To achieve this level of discrimination,

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sophisticated statistical tools such as support vector machines were employed.

A recent study of the isotopic composition of beer [20] examined 33 beers, as a potential source of human body water, and concluded that there was a correlation, albeit not strong, between local drinking water $\delta^2H/\delta^{18}O$ and water from beers purchased at the same location. An earlier study of 160 beers focused on the carbon isotopic composition of the dry residue (comprised mostly of sugars) as a means of determining the addition of C_4 plant material, specifically corn or cane sugar [21]. This study concluded that inexpensive beers and those from large production facilities were most likely to contain detectable quantities of C_4 plant derived carbon, added as a cheap alternative to cereals such as barley or wheat.

In the present study the authors determined the $\delta^2H/\delta^{18}O$ composition of whole beer, the $\delta^{13}C$ composition of the dry residue and the concentrations of a range of cations and anions. The intention was that these data would serve as a background dataset against which beers suspected of being substitute or counterfeit could be compared.

2. Materials and methods

2.1. Sample collection

A total of 162 bottled or canned beers were purchased from licenced retail outlets in the Brisbane metropolitan area (Queensland, Australia) and from on-line retailers. The aim, in collecting these samples, was to represent the largest possible geographical area. The packaging of each sample was examined to verify the authenticity of the product and to confirm the location of manufacture. This information was recorded, together with a general classification as ale, lager, stout or wheat beer.

2.2. Sample preparation

Samples were stored at room temperature and opened immediately prior to analysis. Samples were filtered through hardened ashless paper to remove the majority of the dissolved carbon dioxide and then through a 0.45 μm Durapore filter (Millipore Ireland, Carrigtohill) into two 50 mL sterile containers for cation and anion determination. Degassed samples, intended for δ^2H and $\delta^{18}O$, were dispensed directly into 2 mL auto-sampler vials. For $\delta^{13}C$ analysis, approximately 5 mL of unfiltered beer was heated in a wide beaker at 105 °C until visibly dry.

2.3. Stable isotopic analysis

All isotopic measurements were performed using a Thermo Scientific (Bremen, Germany) Delta V^{PLUS} isotope ratio mass spectrometer (IRMS) coupled to a ConFlo IV interface for working gas introduction and sample dilution. A list of the reference materials used for normalisation is given in Supplementary data.

Hydrogen and oxygen isotopic analysis of liquid samples was performed using a Thermo Scientific Flash 2000 HT elemental analyser (EA) configured for Thermal Conversion (TC/EA) operating at 1400 °C with a helium flow of 100 mL/min introduced via a bottom feed adaptor. Samples (0.15 μL) were introduced by an AS3000 auto-sampler. Six aliquots of beer were injected during each analytical run; the result from the first injection was discounted to allow for memory effects associated with the sample introduction and reactor. The median standard deviations for measurements (n = 5) were 0.4‰ and 0.1‰ for ^2H and ^{18}O, respectively.

Data were normalised to the VSMOW–SLAP scale by two point calibration. A sample of purified Brisbane tap water was analysed throughout the analytical sequence to act as an in-house quality assurance (QA) material and to compensate for any drift in the internal instrument δ-scale.

The ^{13}C composition of solid samples was determined using a Thermo Scientific Flash 2000 HT elemental analyser configured for flash combustion at 950 °C with a helium flow of 100 mL/min. Samples were enclosed in tin capsules (4 × 3.2 mm, IVA, Analysentechnik, Meerbusch, Germany) and introduced into the reactor via a MAS200R auto-sampler. The reactor comprised a single quartz tube containing chrome oxide, reduced copper and silver/cobaltous oxide. A chemical trap containing magnesium perchlorate was inserted between the reactor and the GC column. Each sample was analysed in triplicate with a median standard deviation of 0.04‰.

Data were normalised to the VPDB–LSVEC scale by two point calibration. During the analysis of solid samples, a sample of glucose (Ajax Finechem, Seven Hills, Australia) was analysed throughout the analytical sequence to act as an in-house QA material.

2.4. Cation analysis

Aliquots of approximately 2 g of sample were accurately weighed into PTFE digestion vessels. Four millilitres of high purity nitric acid (69% Seastar Chemicals, Canada) was added to each tube which was then left to stand, at room temperature, overnight to allow slow digestion and gases to evolve. The samples were then sealed and digested using a MD2100 microwave digestion system (CEM, Matthews, USA) with the digestion programme set at 3 stages as follows: stage 1 at power 400 W, temperature 85 °C, time 14 min; stage 2 at power 800 W, temperature 110 °C, time 20 min; stage 3 at power 1600 W, temperature 160 °C, time 10 min. The digested samples were diluted and made up to 40 mL with high purity water (18 mohm, Milli-Q Element System).

Digested samples were analysed using a Vista Pro Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Varian Australia Inc., Vic., Australia) and a 7700 ICP-MS (Agilent Technologies Australia Pty Ltd., Vic., Australia), with auto-sampler and Integrated Sample Introduction System (ISIS). Operating parameters are given in the supplement.

Multi-element and single-element stock standard solutions (10 mg/L) (CHOICE Analytical, NSW, Australia) were used to prepare calibration solutions of 0, 0.1, 1, 10, 100 and 1000 mg/L in 5% HNO_3 for screening of 30 elements. A series of blank values containing 5% HNO_3 reagent (n = 7) were determined and used for blank correction and limits of detection evaluation. Appropriate reference materials and recovery spikes were used for quality control and assurance. Recoveries ranged from 90 to 110% and were deemed satisfactory.

2.5. Anion analysis

Beer samples were diluted 500 fold and transferred to auto-sampler tubes. Phosphate concentrations were determined by reaction with ammonium molybdate and potassium antimony tartrate using a 8500 QuickChem Flow Injection Analyser (Lachat Instruments, WI, USA) with liquid auto-sampler. This was followed by reduction by ascorbic acid to give a molybdophosphoric blue complex, the absorbance of which was recorded at 880 nm.

Other anion concentrations were measured using a Compact IC (Metrohm, Gladesvile, Australia) comprising a 766 automatic sample processor and Dionex separator column types AS22 and AG22. Elution solutions were 4.5 mM sodium carbonate and 0.95 mM sodium bicarbonate. 100 mM sulphuric acid was used as the suppressor reagent. The spike recoveries of anions were used for quality control and ranged from 92 to 100%.

Data were analysed using R 3.0.1 software environment for statistical computing and graphics [22].

3. Results and discussion

The beers obtained for this study are detailed in Table 1 grouped into broad categories based on region of origin (continent) and type (ale,