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- Ponencias Magistrales 27,28 y 29 de noviembre.

PATROCINADO:



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EL USO DE ISÓTOPOS ESTABLES Y PERFILES ELEMENTALES EN LA CARACTERIZACIÓN BOTÁNICA Y GEOGRÁFICA DE LA GOMA ARÁBICA

THE USE OF STABLE ISOTOPES AND ELEMENTAL PROFILES IN THE BOTANICAL AND GEOGRAPHICAL CHARACTERIZATION OF THE ARABIC GUM

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Abstract. Arabic gum (AG) is a dried exudate collected from *Acacia* trees with particular characteristics resulting from its complex mixture of polysaccharides and glycoproteins. It is widely used for food and non-food industries with an increasing global demand so that the determination of AG origin is fundamental to counteract commercial frauds. The study aims to investigate if elemental and isotopic profiles could discriminate, first, between AG produced from plants belonging to the same genus (*Acacia*) but to 2 different species (*A. senegal*, SN; *A. seyal*, SY), and, second, considering only AG of the same botanical origin (SN), between gums produced from different geographic areas (Kordofan region in Sudan vs other Sub-Saharan areas). The principal component analysis (PCA) performed with the significant 22 elements and 3 stable isotopes could clearly separate the 45 gum samples in 2 clusters corresponding to the botanical species. A further PCA, performed using solely the C, N, Cs, Mg and Na content, properly discriminated between SN samples according to their geographic origin, distinguishing the Kordofan ones, produced only in Kordofan region (Sudan) and traditionally renowned as top-quality products.

1 Introduction

Arabic gum (AG; E-Number 414), is definitely the oldest and best known natural gum [1]. It is a dried exudate collected from *Acacia* trees with a total world export of about 102,000 tons/year (annual average 2014–2016) and Sudan being the largest exporter (66% of the total) [2]. Initially, AG was obtained only from *Acacia senegal* (SN) plants, but afterwards, as result of the increased commercial demand, the extraction was extended also to other *Acacia* species. In 1999, the 52nd meeting of the Joint Expert Committee on Food Additives (JECFA) limited its production, defining AG as only the 'dried exudate obtained from the stems and branches of *Acacia senegal* (L.) or *Acacia seyal* (Fam. Leguminosae)' [3]. The two species are native to the semi-arid areas, the so-called gum belt [4]. Considering different botanical source, tree age, climatic conditions and soil environment, which can induce compositional differences in AG [5], Coppen classified the SN products as 1st quality gum, and

SY ones as 2nd quality [6]. Moreover, inside the SN group, the *Acacia senegal* var. *senegal* produced in the Kordofan region (Sudan) and commercially identified as Kordofan gum (SN_{KR}), is traditionally reputed of superior purity and quality.

In 1989, AG was officially recognised as a food additive (E 414) [7], and was finally authorised as a food ingredient by the European Union (Regulation EC No 1333/2008). For what concerned the oenological field, AG is one of the oldest industrial gum approved as a wine additive. There is no legal limit declared, although the International Code of Oenological Practices [8] suggests not exceeding a dosage of 300 mg L⁻¹.

For the botanical discrimination of the *Acacia* gum, the International Organisation of Vine and Wine (OIV) adopted specific approaches based on the specific rotatory power and the total nitrogen (TN) measures (SN solutions must produce negative rotation and have TN between 0.25 - 0.4% (m/m); SY, positive rotation, TN



between 0.10 - 0.20% (m/m)), being the opacity of unrefined or unfresh AG samples the main practical limit for the optical measures (International Oenological Codex, 2000). Recently, Nardin and colleagues [9] proposed an untargeted approach using the liquid chromatography-high resolution mass spectrometry for the discrimination of both botanical and geographical origins.

In this work, we studied the elemental and isotopic composition of 45 AG samples. In particular, were determined 58 macro-, micro- and trace elements, and the stable isotope composition of carbon ($\delta^{13}\text{C}$), nitrogen ($\delta^{15}\text{N}$), oxygen ($\delta^{18}\text{O}$), sulfur ($\delta^{34}\text{S}$) and hydrogen ($\delta^2\text{H}$) in bulk gum due to investigate if the combination of this two different techniques is effective to trace back the botanical and geographical origin of the commercial gum samples.

2 Materials and methods

2.1 Sampling

Thirty SY and 14 SN gum samples (of which, 9 SN_{Other} and 5 SN_{KR}) were provided directly from importers who have guaranteed their authenticity. The exact geographical origin of samples are unknown. A further sample, commercialised as a SN gum mixture (30% SN_{KR} and 70% SN_{Other}) was also used to test the reclassification capability of the proposed model.

2.2 Carbon and nitrogen analysis

About 100 mg of dried sample, weighted in tin foil, were analyzed following manufacturer's instructions. The analysis was performed after dry combustion in excess oxygen using an elemental analyzer (Macro Vario CN, Elementar, Langensfeld, Germany).

2.3 Elemental profile analysis

Before analysis, an acid digestion of the sample was performed using a single reactor chamber microwave (UltraWAVE, Milestone, Shelton, CT, USA) as reported in Bertoldi et al (2014) with minor variations. About 0.7g of sample were weighted in quartz tube, added with 4 ml of nitric acid, and homogenised with microwave-assisted acid digestion. The mineralised solution was then diluted with ultrapure water to the final volume of 13 ml.

Fifty-six macro-, micro- and trace elements (Li, Be, B, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr,

Nd, Sm, Eu, Gd, Dy, Er, Tm, Yb, Re, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th and U) were quantified using an inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7500ce Agilent Technologies, Tokyo, Japan), equipped with a reaction/collision cell in order to remove the principal polyatomic interferences. In detail, He was the collision gas used to analyse Na, Mg, V, Cr, Fe, Ni, Cu, Zn and Eu whereas H₂ was the reaction gas chosen for Ca, Ga and Se. A solution of Sc, Rh and Tb was used as online-added internal standard to correct signal drift. The instrument was tuned daily with a Li, Y, Ce and Tl solution to optimize sensitivity and resolution. Accuracy, tested on reference material NIST 1547 and expressed as recovery percentage, was >75% for all the 34 constituent elements quantified in this study. For assessing the detection limit ($DL=3\sigma$), digested blank samples (reagents only, without sample) were analysed 10 times in a sequence, and, for each element, the standard deviation of the signal was multiplied by 3 (Table 1). The elemental content was expressed on dry weight.

2.4 Stable isotope analysis

The stable isotope ratios of H, C, N, O and S were measured in pure (95%) bulk lyophilized and ground gum sample. This approach is considerably fast and automated (< 10 min for each analysis).

The $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$ and $^{34}\text{S}/^{32}\text{S}$ ratios were measured in one run (around 0.5 mg) using an isotope ratio mass spectrometer (IRMS) (Isoprime, Isoprime Ltd., UK) following total combustion in an elemental analyser (VARIO CUBE, Elementar Analysensysteme GmbH, Germany). The $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ ratios were measured in one run (around 0.5 mg) using an IRMS (Finnigan DELTA XP, Thermo Scientific) coupled with a pyrolyser (Finnigan TC/EA, high temperature conversion elemental analyser, Thermo Scientific).

According to the IUPAC protocol, the values are denoted in delta in relation to the international V-PDB (Vienna-Pee Dee Belemnite) for $\delta^{13}\text{C}$, Air for $\delta^{15}\text{N}$, Cañon Diablo Troilite (V-CDT) for $\delta^{34}\text{S}$ and V-SMOW (Vienna-Standard Mean Ocean Water) for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, according to the following general equation [10]:

$$\delta_i E = \frac{(i \text{ RSA} - i \text{ RREF})}{i \text{ RREF}}$$

where i is the mass number of the heavier isotope of element E, RSA is the respective isotope ratio of the sample and RREF is the relevant internationally recognised reference material. The delta values are multiplied by 1000 and



expressed in units “per mil” (‰). The sample analysis was carried out in duplicate. For $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, the isotopic values were calculated against working in-house standards (protein), which were themselves calibrated against international reference materials. The uncertainty (2 s) of measurements was $<0.3\text{‰}$ for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ analysis and $<1\text{‰}$ for $\delta^{18}\text{O}$, $<3\text{‰}$ for $\delta^2\text{H}$.

3 Results and discussion

3.1. Botanical confirmation of AG samples

According to the International Oenological Codex (International Oenological Codex, 2000) the gum samples were tested for the total nitrogen content in order to confirm the documentary identification provided by the commercial suppliers. The TN content ranged correctly from 0.05 to 0.17% for the SY samples and from 0.25 to 0.59% for the SN ones (Table 1).

3.2 Botanical discrimination of Acacia species

Table 1 reports means and standard deviations of all the analysed parameters.

Regarding the elemental profiles Re (DL = 0.15 ug/kg dw), Ir (DL = 0.4 ug/kg dw), Pt (DL = 1 ug/kg dw) and Au (DL = 0.7 ug/kg dw) were never detected. The total elemental content ranged from 0.4 to 20%, with an average value of 4%. Potassium, Ca e Mg had median content over 1 g/kg, followed by Na, Sr, P, Fe, Rb, Al, Mn, Ba, Cu and Ti with median content between 1 g/kg and 1 mg/kg. Zinc, V, B, Cr, Ni and Mo were between 1 mg/kg and 0.1 mg/kg, whereas other elements (Ce, Co, Nd, As, Li, Y, La, Pb, Cs, Sn, Pr, U, Sm, Gd, Se, Dy, Th, Er, Ga, Tl, Eu, Yb, Sb, Be, Ho, Ge, Cd, Tm, Ag, Pd, Hg, Bi, Te and In) were below 0.1 mg/kg. The contents of As, Cd, Hg and Pb were below the limiting values indicated by OIV [8]. Regarding Fe, 10% of samples were above the limit of 60 mg/kg dw. Regarding the C content, it ranged from 31.5 to 39.3% for SY samples and from 32.9 to 40.6% for SN, showing a slight significance in the discrimination between the two species ($p=0.014$).

Concerning stable isotope ratio analysis, AG showed $\delta^{13}\text{C}$ values ranging from -25.8 to -22.9‰ varying considerably ($p<0.01$) between the two species considered with lower values for SY (average -25.4‰) and higher for SN (average -23.8‰). This behaviour is in line with the botanical origin of the matrix, indeed while C4 plants have $\delta^{13}\text{C}$ values between -14 and -12‰,

C3 plants (such as the legume species Acacia) range from -30 to -23‰ [11-12].

The isotopic variation does not seem correlate with the species (SY vs SN) but rather with the environmental condition of growth, in fact, as reported by [13] tree-rings of SY and SN cultivated together in the same experimental area in Ethiopia with an average annual precipitation ranges between 550 and 900 mm don't show significant difference each other in the isotopic composition. Plants normally exhibit higher $\delta^{13}\text{C}$ values when high temperatures, low air humidity and a high ground-water deficit lead to narrower stomatal apertures in the leaves of plants [14]. In addition, $\delta^{13}\text{C}$ is very sensitive to soil water deficiency [15]. SN is very drought-resistant and tolerant of high daily temperature. It normally grows in areas with a long dry period and a maximum of 300-400 mm rain/year whereas SY is most common in areas with 500-1200 mm rain/year and subject to waterlogging [16]. This differentiated climate adaptation could explain the different isotopic range of $\delta^{13}\text{C}$. $\delta^{13}\text{C}$ is partially correlated also with a different altitude of the growing area. This could have a contribution on the isotopic composition of SY that can grow at higher altitude (up to 2000 m a.s.l.) than SN (between 100-1700 m).

$\delta^{15}\text{N}$ of AG ranged between -0.8‰ and +3.5‰ significantly lower than values previously reported [17]. SY gum has lower value, even negative ones (on average -0.80‰), compared with the SN gum (on average 0.08‰). $\delta^{15}\text{N}$, that is measured on gum's amino acids and proteins, is mainly determined by the primary sources, namely fertilizers, ammonium and nitrate and N_2 from nitrogen assimilation. SN and SY belong to the family of Leguminosae (known also as Fabaceae), known for hosting rhizobia bacteria within structures on roots called root nodules. These bacteria create with the host plant a symbiotic relationship through which they fix atmospheric N_2 in assimilable NH_4^+ that plant will embody into organic compounds such as amino acids, in exchange for carbohydrates and other organic compounds. The N fixation and metabolization of fixed N in nodules leads to isotopic fractionation which is at the base of negative values of $\delta^{15}\text{N}$ values in transported N. According to Ndoye and [18], among Acacia species there are differences in N_2 fixation and SY was clearly the best in total N fixed having a high N_2 fixing potential (NFP) while the other Acacia species had a low one.

The texture of the soil is a crucial variable for N fixation too, and following the work by [19], the contribution of fixed N to foliage growth in SN was highest in the Rahad sand-soil provenance and lowest in the Mazmoom clay-soil provenance. Furthermore in the proteins



themselves the amide-N is relatively enriched in ^{15}N compared to that of α -amino-N and the amino acids show the following ^{15}N enrichment pattern: aspartic acid/asparagine > glutamic acid/glutamine > threonine, proline, valine > glycine + alanine + serine, γ -aminobutyric acid and phenylalanine [20]. Considering the different chemical composition of the two AG, the one obtained from SN has higher protein and amino acids content, in particular it has nearly 40% more aspartic acid, 30% more glutamic acid and 24% more threonine [21].

The $\delta^2\text{H}$ values ranged from -55 to -29‰ for SY and from -41 to -24‰ for total SN. These values are similar to those reported by [17] between -63 and -34‰ for $\delta^2\text{H}$. Different components of gum derived from different biosynthetic pathway and therefore they have different isotopic composition of hydrogen [22] that seems to give an important contribute for a good distinction between SY and SN with the highest values for the latter (average -36‰ vs -43‰) despite a partial overlap of the populations. SN and SY could grow on different altitudes, this difference could lead to an explanation on why the $\delta^2\text{H}$ is different between the two species. Dansgaard and colleagues [23] demonstrated that the observed geographic distribution in isotope composition is related to a number of environmental parameters that characterize a given sampling site, such as latitude, altitude, distance to the coast, amount of precipitation, and surface air temperature [24]. In particular the $\delta^2\text{H}$ decreases with altitude due to isotopic fractionation linked with the evaporation of water which cause a ^2H depletion in rain's water molecule.

Considering the high number of the studied analytical parameters, PCA was performed using only significant variables (Kruskal-Wallis test, $p < 0.01$; Table 1) [25]. The biplot (Figure 1; squares = SN; circles = SY) highlighted how the samples could be clearly separated into two groups according to the species. All the SN samples were in the top quadrants and all the SY samples in the bottom ones. Together, the first two dimensions explained 69.5% of variance, with 50.9% explained by Factor 1 (F1) and 18.6% by Factor 2 (F2). Among the variables, as shown in the biplot (Figure 1), most of them are positively or negatively correlated, in particular the rare earth elements that are positively correlated ($r > 0.85$; Person test). Considering the squared cosines of variables, the rare earth elements, U, Mo and Pd resulted well linked with the F1 reporting a squared cosine (SC) that ranged from 0.97 to 0.59, while on F2 only $\delta^{13}\text{C}$ reported a SC higher than 0.5 (SC=0.67). Other F2 important variables were Rb, Mg, and B with a SC of 0.48, 0.47 and 0.38 respectively.

This representation shows clearly that the 2 *Acacia* species are well discriminated by combining the elemental profile with the stable isotopic ratio of gum samples. These elements, and in particular B, Sr, Ba, Mg, Mo, U and rare earth elements, were previously selected by other statistical models and indicated as useful for botanical discrimination for honey [26], tannins [27], coffee [27] and grapes [28].

Table 1. Statistical distribution (mean, std deviation) of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$, D/H, $\delta^{18}\text{O}$ and mineral elements in arabic gum samples grouped by species.

| Parameter | Unit of measurement | <i>A. senegal</i> | | <i>A. seyal</i> | |
|-----------|---------------------|-------------------|----------------|-----------------|----------------|
| | | Mean | Std. deviation | Mean | Std. deviation |
| Li | mg/kg dw | 48.0 | 26.7 | 36.0 | 14.7 |
| Be | mg/kg dw | 2.10 | 2.67 | 2.52 | 1.82 |
| B** | mg/kg dw | 0.97 | 0.51 | 0.60 | 0.23 |
| Ti | mg/kg dw | 1.34 | 2.22 | 1.41 | 1.02 |
| V* | mg/kg dw | 2.15 | 6.17 | 1.64 | 1.53 |
| Cr | mg/kg dw | 0.39 | 0.43 | 0.58 | 0.56 |
| Mn** | mg/kg dw | 21.3 | 48.2 | 2.87 | 1.38 |
| Fe** | mg/kg dw | 2364 | 9097 | 36.3 | 26.2 |
| Co | mg/kg dw | 110.4 | 153.5 | 47.3 | 22.0 |
| Ni | mg/kg dw | 0.33 | 0.26 | 0.32 | 0.32 |
| Cu | mg/kg dw | 1.89 | 1.64 | 1.37 | 0.54 |
| Zn | mg/kg dw | 0.95 | 0.76 | 0.78 | 0.35 |
| Ga* | mg/kg dw | 3.90 | 4.77 | 5.89 | 4.61 |
| Ge | mg/kg dw | 4.58 | 8.69 | 1.47 | 0.92 |
| As | mg/kg dw | 0.09 | 0.19 | 0.05 | 0.04 |
| Se | mg/kg dw | 13.2 | 14.0 | 7.82 | 3.10 |
| Rb** | mg/kg dw | 14.7 | 8.43 | 7.49 | 2.91 |
| Sr** | mg/kg dw | 123 | 145 | 55.7 | 36.3 |
| Y** | mg/kg dw | 26.6 | 34.7 | 45.6 | 25.2 |
| M** | mg/kg dw | 208 | 682 | 218 | 194 |
| Pd** | mg/kg dw | 0.30 | 0.34 | 0.63 | 0.37 |
| Ag* | mg/kg dw | 0.77 | 1.07 | 0.77 | 0.52 |
| Cd | mg/kg dw | 1.52 | 2.69 | 1.10 | 0.64 |

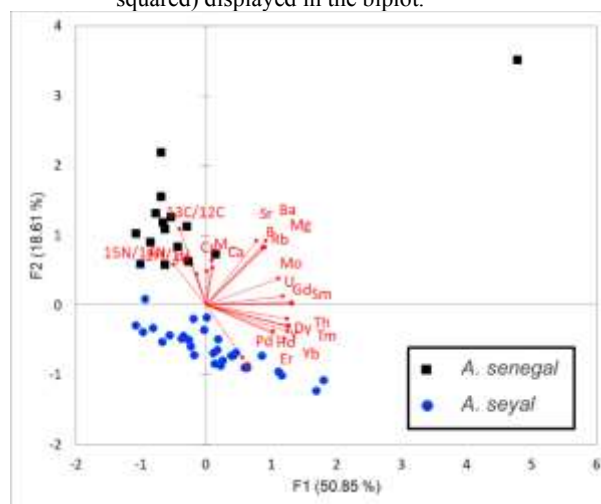


| | | | | | |
|------|----------|-------|------|-------|------|
| In | mg/kg dw | 0.70 | 2.71 | 0.27 | 0.63 |
| Sn* | mg/kg dw | 248 | 911 | 112 | 220 |
| Sb | mg/kg dw | 30.7 | 98.7 | 4.47 | 5.87 |
| Te | mg/kg dw | 0.38 | 0.82 | <0.26 | 0.19 |
| Cs** | mg/kg dw | 31.4 | 23.2 | 13.9 | 11.3 |
| Ba** | mg/kg dw | 60.0 | 135 | 8.23 | 16.7 |
| La | mg/kg dw | 81.5 | 175 | 44.3 | 34.1 |
| Ce | mg/kg dw | 109 | 220 | 96.2 | 67.6 |
| Pr* | mg/kg dw | 13.8 | 26.7 | 13.7 | 8.22 |
| Nd* | mg/kg dw | 50.2 | 96.1 | 56.0 | 33.2 |
| Sm** | mg/kg dw | 9.25 | 15.9 | 12.5 | 7.32 |
| Eu | mg/kg dw | 7.58 | 17.1 | 3.81 | 2.23 |
| Gd** | mg/kg dw | 8.73 | 14.4 | 12.0 | 6.93 |
| Dy** | mg/kg dw | 5.16 | 6.93 | 9.10 | 5.24 |
| Ho** | mg/kg dw | 1.20 | 1.24 | 1.90 | 1.01 |
| Er** | mg/kg dw | 2.72 | 3.28 | 4.92 | 2.71 |
| Tm** | mg/kg dw | 0.56 | 0.43 | 0.81 | 0.37 |
| Yb** | mg/kg dw | 2.08 | 2.42 | 4.10 | 2.24 |
| Re | mg/kg dw | <0.15 | - | <0.15 | - |
| Ir | mg/kg dw | <0.4 | - | <0.4 | - |
| Pt | mg/kg dw | <1 | - | <1 | - |
| Au | mg/kg dw | <0.7 | - | <0.7 | - |
| Hg | mg/kg dw | 0.57 | 0.68 | 0.41 | 0.53 |
| Tl | mg/kg dw | 4.32 | 2.79 | 3.88 | 2.19 |
| Pb | mg/kg dw | 29.9 | 41.0 | 19.9 | 15.0 |
| Bi | mg/kg dw | 0.55 | 0.69 | 0.25 | 0.22 |
| Th** | mg/kg dw | 5.91 | 8.74 | 10.52 | 6.09 |
| U** | mg/kg dw | 12.8 | 29.3 | 17.8 | 15.5 |
| Al* | mg/kg dw | 7.25 | 11.9 | 12.2 | 10.3 |
| Ca** | g/kg dw | 8.25 | 9.97 | 3.95 | 3.25 |
| K | g/kg dw | 14.4 | 10.3 | 24.3 | 17.1 |
| Mg** | g/kg dw | 2.53 | 1.89 | 1.18 | 0.43 |
| Na | g/kg dw | 5.12 | 7.03 | 6.56 | 9.21 |

| | | | | | |
|--------|--------------|-------|------|-------|------|
| P** | mg/kg dw | 18.7 | 12.1 | 43.8 | 15.5 |
| d13C** | ‰, vs V-PDB | -23.8 | 0.42 | -25.3 | 0.34 |
| d15N** | ‰, vs AIR | 1.78 | 1.17 | 0.66 | 0.72 |
| d2H** | ‰, vs V-SMOW | -35.5 | 5.22 | -43.1 | 7.32 |
| d18O** | ‰, vs V-SMOW | 37.4 | 0.97 | 36.4 | 1.44 |
| d34S | ‰, vs CDT | 2.77 | 5.54 | 2.38 | 4.45 |
| C* | % | 37.4 | 2.63 | 35.5 | 2.69 |
| N** | % | 0.33 | 0.08 | 0.10 | 0.03 |

Note: ** = p<0.01; * = p<0.05; n.s. = not significant (Kruskal-Wallis test)

Figure 1. Principal component analysis (PCA) of arabic gum samples (*A. seyal* = circle; *A. senegal* = squared) displayed in the biplot.



3.3 Kordofan samples discrimination

Considering only the SN samples (SN_{KR} and SN_{Other}), the Kruskal-Wallis test (p<0.05; Table 1) selected new significant variables: Na and Cs were more present in SN_{KR} samples, while Mg and C% were more concentrated in SN_{Other}. PCA was performed using significant variables (p<0.01), including TN, that was never before proposed for the geographical origin discrimination of AG. Figure 3 shows the score and loading plots of the SN samples (blue squares = SN_{Other}; white squares = SN_{KR}; black square = mixture sample (70 SN_{Other}:30 SN_{KR})). Together, the first two dimensions explained 83.4% of variance, with 61.7% explained by F1 and 21.7% by F2, and the samples were clustered in two groups according to the geographical origin. SN_{KR} samples, produced in a limited Sudan region, were closely grouped on the left side of the quadrants, while SN_{Other} samples,



gathered from different African regions, were all on the right side, but more scattered. To confirm this discriminatory capacity of this variables, the sample commercially declared as a mixture of 70% SN_{other} and 30% SN_{KR} was graphically positioned between the 2 main groups of pure samples. Na and Cs, but also Mg, even not completely significant in our study ($p = 0.028$), were already reported to be useful in the geographic characterisation of various agro-products such as saffron [29], wine [30], wheat and cocoa [31].

Table 2. Statistical distribution (mean, std deviation) of $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$, D/H, $\delta^{18}O$ and mineral elements in arabic gum samples grouped by geographical origin.

| Parameter | Unit of measurement | Senegal-Kordofan | | Senegal-other | |
|-----------|---------------------|------------------|----------------|---------------|----------------|
| | | Mean | Std. deviation | Mean | Std. deviation |
| Li | mg/kg dw | 54.5 | 6.42 | 44.2 | 34.4 |
| Be | mg/kg dw | 3.06 | 3.52 | 1.56 | 2.32 |
| B | mg/kg dw | 1.00 | 0.09 | 0.94 | 0.67 |
| Ti | mg/kg dw | 0.68 | 0.25 | 1.81 | 2.82 |
| V | mg/kg dw | 0.43 | 0.16 | 3.30 | 7.94 |
| Cr | mg/kg dw | 0.29 | 0.11 | 0.30 | 0.25 |
| Mn | mg/kg dw | 6.25 | 2.73 | 31.0 | 61.6 |
| Fe | mg/kg dw | 9.52 | 3.28 | 393.2 | 11743 |
| Co | mg/kg dw | 49.2 | 20.0 | 148 | 192 |
| Ni | mg/kg dw | 0.22 | 0.03 | 0.33 | 0.26 |
| Cu | mg/kg dw | 1.42 | 0.07 | 2.17 | 2.11 |
| Zn | mg/kg dw | 1.23 | 0.91 | 0.82 | 0.72 |
| Ga | mg/kg dw | 2.30 | 0.90 | 4.92 | 6.04 |
| Ge | mg/kg dw | 1.21 | 0.81 | 6.87 | 10.82 |
| As | mg/kg dw | 43.2 | 33.4 | 131 | 242 |
| Se | mg/kg dw | 10.4 | 5.11 | 14.9 | 17.9 |
| Rb | mg/kg dw | 16.8 | 3.74 | 13.6 | 10.6 |
| Sr | mg/kg dw | 95.2 | 41.3 | 142 | 187 |
| Y | mg/kg dw | 22.1 | 16.5 | 29.5 | 44.1 |
| Mo | mg/kg dw | 30.1 | 32.3 | 326 | 879 |
| Pd | mg/kg dw | 0.32 | 0.16 | 0.30 | 0.44 |

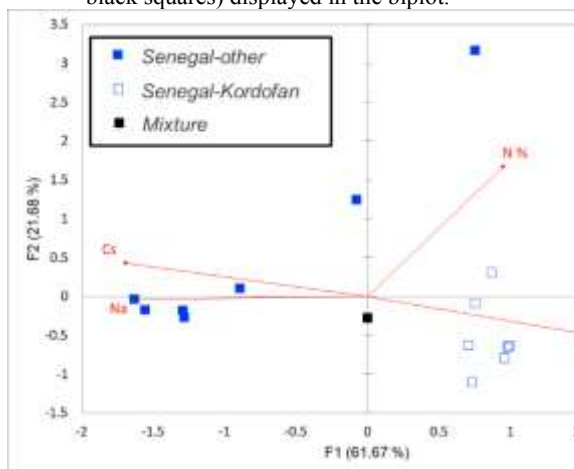
| | | | | | |
|------|----------|-------|------|-------|--------|
| Ag | mg/kg dw | 0.35 | 0.17 | 1.00 | 1.34 |
| Cd | mg/kg dw | 0.88 | 0.53 | 1.93 | 3.47 |
| In | mg/kg dw | <0.18 | - | 1.16 | 3.49 |
| Sn | mg/kg dw | 10.9 | 4.94 | 407 | 1175 |
| Sb | mg/kg dw | 4.84 | 3.95 | 47.3 | 127.54 |
| Te | mg/kg dw | 0.28 | 0.33 | 0.49 | 1.05 |
| Cs** | mg/kg dw | 60.1 | 10.5 | 16.1 | 9.92 |
| Ba | mg/kg dw | 14.5 | 10.2 | 90.5 | 171 |
| La | mg/kg dw | 29.5 | 9.39 | 117 | 224 |
| Ce | mg/kg dw | 46.8 | 15.0 | 151 | 283 |
| Pr | mg/kg dw | 6.44 | 2.61 | 18.7 | 34.3 |
| Nd | mg/kg dw | 24.6 | 11.2 | 66.9 | 123.74 |
| Sm | mg/kg dw | 5.42 | 2.58 | 11.8 | 20.5 |
| Eu | mg/kg dw | 2.62 | 0.90 | 10.8 | 22.0 |
| Gd | mg/kg dw | 5.35 | 3.07 | 10.9 | 18.6 |
| Dy | mg/kg dw | 4.25 | 2.82 | 5.79 | 8.89 |
| Ho | mg/kg dw | 1.07 | 0.57 | 1.30 | 1.58 |
| Er | mg/kg dw | 2.42 | 1.67 | 2.92 | 4.16 |
| Tm | mg/kg dw | 0.55 | 0.25 | 0.57 | 0.54 |
| Yb | mg/kg dw | 2.08 | 1.57 | 2.10 | 3.00 |
| Re | mg/kg dw | <0.15 | - | <0.15 | - |
| Ir | mg/kg dw | <0.4 | - | <0.4 | - |
| Pt | mg/kg dw | <1 | - | <1 | - |
| Au | mg/kg dw | <0.7 | - | <0.7 | - |
| Hg | mg/kg dw | 0.57 | 0.57 | 0.61 | 0.79 |
| Tl | mg/kg dw | 5.31 | 1.34 | 3.82 | 3.43 |
| Pb | mg/kg dw | 21.9 | 14.2 | 36.5 | 52.1 |
| Bi | mg/kg dw | 0.45 | 0.42 | 0.64 | 0.85 |
| Th | mg/kg dw | 4.62 | 1.42 | 6.76 | 11.42 |
| U | mg/kg dw | 8.62 | 7.56 | 16.1 | 38.0 |
| Al | mg/kg dw | 3.63 | 3.05 | 9.76 | 14.9 |
| Ca | g/kg dw | 4.76 | 2.81 | 10.3 | 12.5 |
| K | g/kg dw | 16.9 | 11.2 | 12.9 | 10.8 |



| | | | | | |
|----------|------------------|---------------|------|---------------|------|
| Mg* | g/kg dw | 2.3 3 | 0.22 | 2.6 4 | 2.49 |
| Na* | g/kg dw | 12. 9 | 7.01 | 0.7 0 | 1.41 |
| P | mg/kg dw | 16. 8 | 8.49 | 19. 7 | 14.7 |
| d13 C | ‰, vs V- PDB | - 24. 0 | 0.26 | - 23. 7 | 0.49 |
| d15 N | ‰, vs AIR | 1.3 5 | 0.93 | 2.1 3 | 1.25 |
| d2H | ‰, vs V- SMOW | - 36. 9 | 2.99 | - 33. 9 | 5.66 |
| d18 O | ‰, vs V- SMOW | 37. 7 | 0.29 | 37. 1 | 1.14 |
| d34 S | ‰, vs CDT | 1.0 7 | 3.80 | 3.6 6 | 6.62 |
| C** | % | 34. 6 | 1.14 | 39. 4 | 1.01 |
| N** | % | 0.2 7 | 0.01 | 0.3 6 | 0.09 |

Note: ** = $p < 0.01$; * = $p < 0.05$; n.s. = not significant (Kruskal-Wallis test)

Figure 2. Principal component analysis (PCA) of arabic gum samples (*A. senegal* gum of general origin (Senegal-other) = blue squares; Kordofan gums (Senegal-Kordofan) = white squares; Mixture sample (30% Senegal-Kordofan +70% Senegal-other) = black squares) displayed in the biplot.



4 Conclusions

Combined analyses of trace element and isotopic contents provide an effective method for the quality control of food ingredients. 22 elements and 3 stable isotopes have resulted particularly significant in discriminating between arabic gum produced from SN and SY. Furthermore, the evaluation of C%, N%, Cs, Mg and Na content made it possible to discriminate, inside the SN group, the Kordofan gum samples, produced in a restricted area of Sudan and recognised of particular quality.

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