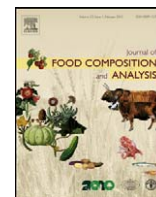




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## Original Article

## Elemental and isotopic characterization of cane and beet sugars

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## ABSTRACT

An interlaboratory program designed to assess the feasibility of using multi-element and isotopic measurements for determining the geographic origin of sugars permitted an intercomparison of the performance (in terms of limits of detection, reproducibility and bias) of various analytical techniques: inductively coupled plasma (ICP)-optical emission spectrometry (OES); different variations of ICP-mass spectrometry (MS): quadrupole (QMS), sector-field (SFMS) and multi-collector (MC-ICP-MS); thermal ionization MS (TIMS); and isotope ratio MS (IRMS). These various methods were applied to cane (raw and refined) and beet (refined) sugars from different origins. Concentrations of 63 elements and isotope ratios of Pb, Sr and C in sugar samples are reported. Determining the geographic origin of sugars appears feasible using elemental fingerprinting.

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## 1. Introduction

Interest in the inorganic analysis of sugars exists in many fields of human activity and stems from different factors. First, sugar plays a fundamental role in the diet of humans, with annual consumption in the range of 25–60 kg for adults. Therefore, determination of the elemental composition of sugar is important in nutrition studies for assessment of intake doses of micronutrients and toxic elements. For example, Jorhem and Sundström (1993) included sugar in a survey of food products on the Swedish market. There is also a series of

studies by Sancho et al. (1997, 1998, 2000) devoted to the determination of As, Cd, Co, Cu, Ni, Pb and Zn by anodic stripping voltammetry (ASV) in refined beet sugar. These authors predicted that, though present levels of toxic elements allowed by European legislation in refined sugar are in the  $\mu\text{g g}^{-1}$  range, it is likely that these levels will be lowered in the near future. More recently, Santos et al. (2004) reported concentrations of nine elements (Al, Cd, Cr, Cu, Mn, Ni, Pb, U and Zn) in sugar for assessment of the daily intake of trace elements due to consumption of foodstuffs by inhabitants of Rio de Janeiro. Furthermore, sugar quality, and hence price, are closely related to elemental contents.

There are also several reports on trace element contents in sweets and other sugar-based products (Canuto et al., 2003; Naqvi et al., 2004). Studies on the transfer of chemical contaminants through the food chain can provide useful information for the

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development of surveillance programs aimed at ensuring the safety of the food supply and minimizing human exposure to toxic agents (Bayat et al., 1995; Biego et al., 1998; Dolan and Capar, 2002; Lombardi-Boccia et al., 2003).

Secondly, there are correlations between trace element content in soils and in unprocessed sugars, making sugar analysis useful in environmental studies. Moreover, such analyses are important to the sugar producing and refining industries. Thus, variations in trace element contents in the products formed during the successive stages of sugar processing, as well as correlations between chemical composition of cane sugars and soils in varying environmental conditions, have been the focus of attention in several studies (Awadallah et al., 1984, 1985, 1986; Mohamed, 1999). More than 40 elements were determined using a combination of instrumental neutron activation analysis (INAA), atomic absorption spectrometry (AAS) and ICP-OES.

Thirdly, enforcement of international trade regulations may require provenance determination of sugars, which can be accomplished by elemental fingerprinting or stable isotope analysis. Trace element composition and isotope ratios of foods reflect the local environment (geographical area of origin), as well as impurities related to specific food processing and packaging techniques. During the last few years, inorganic and isotope analyses have been frequently used for fingerprinting, authenticity evaluation and provenance studies involving a great variety of food products, including wines (Barbaste et al., 2002; Larcher et al., 2003; Kokkinofa et al., 2003; Taylor et al., 2003), honey (Latorre et al., 2000), cheese (Fortunato et al., 2004) and caviar (Rodushkin et al., 2007). Such fingerprinting could have both legal and regulatory utility.

However, in spite of the need for accurate inorganic analyses of sugars, there are no matrix matched reference materials that can be used for establishing and maintaining the reliability of analytical procedures. Though white sugar was listed among 11 candidate agricultural reference materials under preparation over 20 years ago (Ihnat, 1988) – a certification campaign that resulted in the production of materials certified for 34 elements – this particular matrix was ultimately excluded from subsequent publications (Tanner et al., 1988; Ihnat, 2000a,b; Sharpless et al., 2004). This is probably a reflection on analytical difficulties associated with analyses at ultra-trace levels in refined sugars. For stable isotope analysis, only two reference materials are available: SRM 8542 from the US National Institute of Standards and Technology (NIST) and IAEA-C6 from the International Atomic Energy Agency (IAEA), both having a sucrose matrix, certified for  $\delta^{13}\text{C}$ .

The NITECRIME (Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics) Forensic Network, an international collaborative research network, was established to investigate and promote the use of trace elements and isotope ratios in examinations of materials of forensic interest in matters of fraud, crime and trade. The Network includes research centers in Europe, Australia and the US, including government research and forensic organizations and university research laboratories. In 2003, the NITECRIME Network initiated an interlaboratory exercise aimed at assessing the performance of different analytical techniques for measuring element and isotope levels in sugars in order to determine their geographic origin. During this project, sugar samples (cane and beet, raw and refined) representing several sugar exporting countries were distributed among collaborating laboratories for elemental and isotopic analyses within their expertise. This paper summarizes the findings of this study.

## 2. Samples

Authentic cane and beet sugars originating from different geographical locations were obtained by US Customs and Border

Protection from sugar companies in the US and Europe, aliquoted and distributed to nine participating laboratories as blind samples. Eight beet sugar samples were obtained from Moldova (Drochia), Poland (Raciborz), USA (Idaho and Michigan), Netherlands, France (Epeville), Germany (Gross-Gerau), and Hungary (Szerencs). Beet sugar samples, commercially classified as refined beet sugar, were in the form of fine, white crystals of highly purified sucrose. Four cane sugar samples were obtained from USA (Louisiana), Costa Rica, Argentina and Swaziland. Cane sugar samples, commercially classified as raw cane sugar, were in the form of coarse, brown crystals of unrefined sucrose. IAEA-C6 and Ultrex grade sucrose (J.T. Baker, Phillipsburg, NJ, USA) were also included, the former as a reference standard for  $\delta^{13}\text{C}$  measurements and the latter as a matrix blank. NIST SRM 987 and 981 were used as isotope reference materials for Sr and Pb isotope ratio measurements, respectively.

## 3. Materials and methods

Sample preparation routines tested during the first round (2003) for elemental analysis included both simple dissolution of sugar and wet digestions (open vessels and microwave-assisted, MW) using various acids or acid mixtures ( $\text{HNO}_3$ ,  $\text{HNO}_3 + \text{H}_2\text{O}_2$ , aqua regia, aqua regia + HF), prior to replicate analysis by ICP-SFMS.

In the second round of the program (2004), participants were asked to analyze 12 sugar samples, IAEA-C6 and Ultrex sucrose, using a standardized sample preparation procedure. This required simple dissolution of 0.5 g sugar in 0.14 M  $\text{HNO}_3$ , with five separate preparations of each sample. The list of mandatory elements included Al, B, Ba, Ca, Co, Cr, Cs, Cu, Fe, Li, K, Mg, Mn, Na, Ni, Pb, Rb, Sn, Sr, Ti, V and Zn, though concentrations of many additional elements were also reported.

Sample preparation protocols for isotopic ratio measurements were not standardized during the study, as they are strongly technique-specific. For Pb isotopes, simple dilution of the solutions obtained as described above was sufficient; ratios were measured by ICP-SFMS using NIST SRM 981 as the reference material. For  $^{13}\text{C}$ , little sample preparation was required (Leblebici, 2009); roughly 2–3 mg dried, pulverized sugar or 0.5–1  $\mu\text{L}$  of concentrated sugar syrup (sugar dissolved in de-ionized water at 1:1 ratio) was weighed into a 3.5 mm  $\times$  5 mm tin capsule and combusted in an elemental analyzer linked to the isotope ratio mass spectrometer; IAEA-C6 was used as the reference material. For Sr isotopes, highly precise measurements required separation of the analyte from the sample matrix and interfering elements, especially Rb, Ba and Ca (Rodushkin et al., 2007). Approximately 0.5 g of sample was weighed into a quartz crucible and ashed in a muffle furnace at 850  $^\circ\text{C}$  for 5 h. The ash was dissolved in concentrated  $\text{HNO}_3$ , evaporated to dryness and redissolved in 3 mL of 3 M  $\text{HNO}_3$ . For the chemical separation, the redissolved samples were loaded onto small columns containing 50  $\mu\text{L}$  Sr-specific resins and washed with 3 M  $\text{HNO}_3$  to elute interfering elements. The fraction containing Sr was then eluted with 0.05 M  $\text{HNO}_3$ . NIST SRM 987 was used as the reference material.

## 4. Results and discussion

### 4.1. Preliminary studies

During the first round of the program, the participants were requested to analyze three raw cane sugar samples for as many analytes as possible using sample preparation techniques and analytical methods of their own choosing. The latter included ICP-OES, ICP-QMS and ICP-SFMS for element concentrations, and IRMS, TIMS, ICP-SFMS and MC-ICP-MS for isotope ratio measurements. It

should be noted that none of the cooperating laboratories used analytical methods recommended by ICUMSA (International Commission for Uniform Methods of Sugar Analysis, 1994), such as spectrophotometry or electrothermal AAS. The former technique lacks the necessary sensitivity to determine inorganic impurities at trace and ultra-trace levels, and the latter requires removing sample matrix to prevent strong interferences (Sancho et al., 1998). Although other methods such as flame AAS (FAAS), ASV and INAA are efficient in determining low levels of certain elements, the popularity of analytical techniques used in the present program for agricultural/food matrices is constantly growing. This is mainly due to the combination of multi-element capabilities, speed of analysis, low detection limits, and, for MS-based techniques, isotopic capabilities.

However, one must not forget that spectral interferences have the ability to severely affect the accuracy of the analytical results and therefore have been frequently referred to as the Achilles' heel of ICP-QMS. Taylor et al. (2005) recently reported observing pronounced polyatomic ion signals in ICP-MS spectra of solutions containing 1–3% glucose, fructose, and sucrose. They suggested that sugar-derived molecular species have the ability to survive the plasma, giving rise to polyatomic ions interfering with numerous analytes in the mass range 60–181 amu. Selected spectral interferences occurring in a sugar matrix (100 fold dilution with 0.14 M HNO<sub>3</sub>) are shown in Fig. 1. It is obvious that, of the isotopes shown, only Ni will have a fair chance of being accurately determined using the <sup>62</sup>Ni isotope, unless the higher mass resolution capabilities of ICP-SFMS are applied.

Traditional sample introduction to the ICP by solution nebulization requires conversion of solid samples into solutions. Fecher and Ruhnke (2002) demonstrated risks for losses of volatile analytes and for cross-contamination during dry ashing of white sugar, a procedure frequently used for sugar mineralization in the past. Preparation of sugars for analysis by simple dissolution is appealing (Sancho et al., 1997, 1998, 2000), as it eliminates volatile element loss associated with ashing/open-vessel digestion techniques, minimizes contamination by reagents and the laboratory environment, as well as improves cost and time efficiency (provenance studies may require analysis of large numbers of samples). However, there is an accompanying risk for incomplete analyte recovery.

For the majority of analytes tested, results of first round analyses indicated that simple dissolution of sugar in 0.14 M HNO<sub>3</sub> provided concentrations indistinguishable from those obtained by MW-assisted digestion with an aqua regia + HF mixture. Notably higher concentrations were observed after the latter sample preparation only for Si, Al, Fe, W and Zr—elements most probably associated with silicate-based soil contamination of sugars. However, the presence of even minute quantities of HF in the digestion mixture requires the use of a HF-resistant sample introduction system to control otherwise severe blank contributions from parts made of glass or quartz. Owing to more extensive sample handling, higher reagent consumption and the use of non-disposable digestion vessels, method limits of detection (LODs) are inferior for digestion procedures than for simple dissolution by virtue of higher preparation blanks. This is especially pronounced for highly sensitive techniques such as ICP-QMS and ICP-SFMS.

The minimum representative sub-sample size was determined by triplicate analyses of increasing aliquots (mass range 20 mg–2 g) of raw cane sugar followed by analysis by ICP-SFMS. For the majority of elements present in the sugar at detectable concentrations, there were no differences in RSD between different sample sizes, thus confirming homogeneity of the sugar samples. However, for Fe, Sn and the rare earth elements (REE), decreases in sample size below 0.5 g resulted in depreciating repeatability.

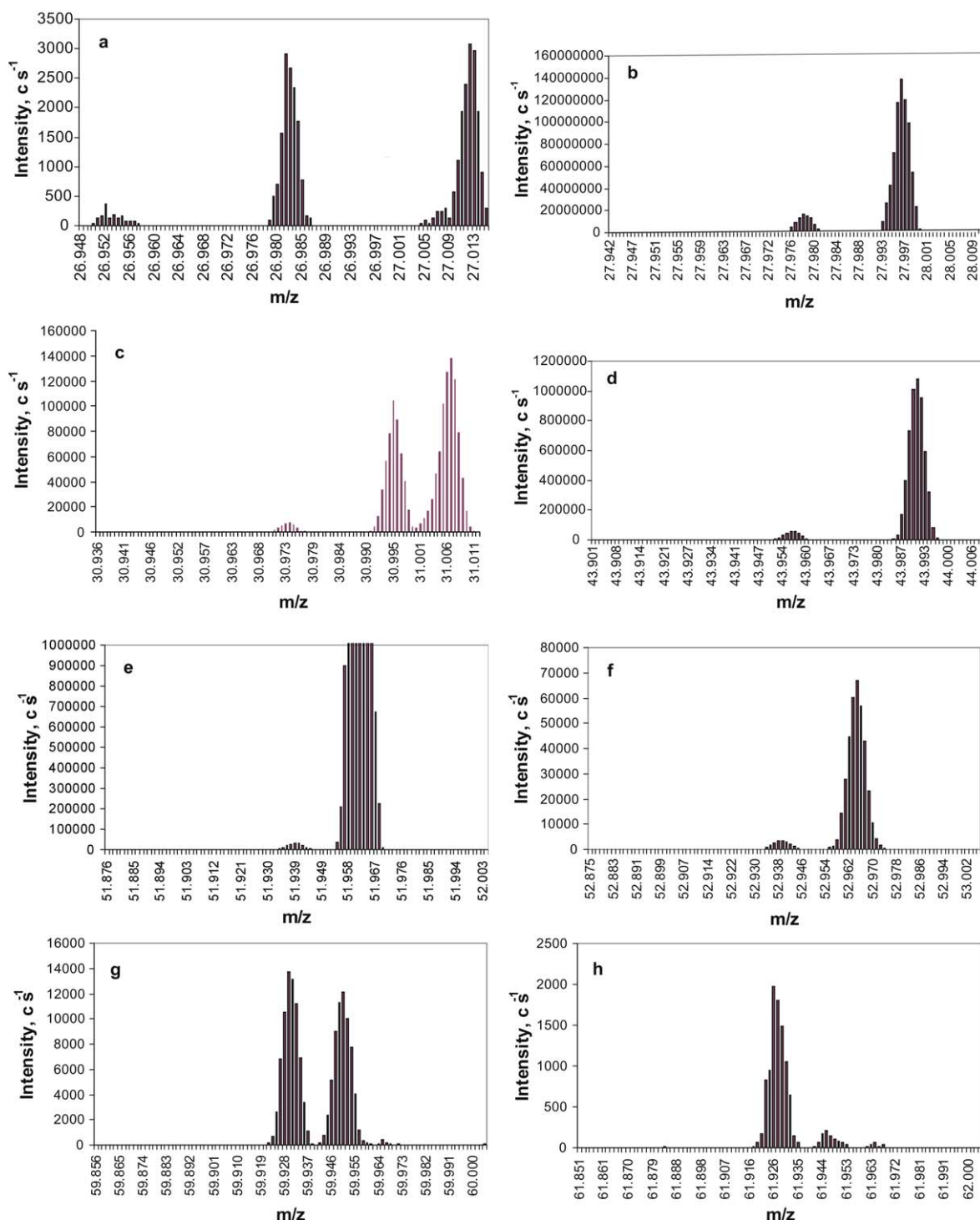
#### 4.2. Multi-element analysis

Table 1 summarizes data on the analytical performance obtained during the second round of the program. Elements are arranged in order of decreasing mean concentrations found in the sugar samples during this study. As a rule, method LODs increase in the order ICP-SFMS < ICP-QMS < ICP-OES. The lowest LODs reported by participating laboratories were below 1 ng g<sup>-1</sup> for 56 elements and compare favorably with the lowest LODs reported for sugar samples in the literature. Au, Ir, Ge, Os, Pd, Pt, Rh and Ru were undetectable in all sugar samples, with corresponding LODs in the low pg g<sup>-1</sup> range, except for Ge at 0.5 ng g<sup>-1</sup>. For platinum group elements this may partly be explained by limited solubility in 0.14 M HNO<sub>3</sub>. Though nine laboratories reported results, the degree of completeness of data sets returned varied greatly between participants. It should be noted that only results above respective LODs were considered. For six elements (K, Ca, Mg, Na, Fe and Sr), all participating laboratories were able to detect concentrations in at least one sample. For 24 elements, at least three complete data sets were submitted. In some sugars, mainly refined beet sugars, Si, B, Se, As, I, Li, Y, Ga, Sc, REE, Te, Th, Nb, Hg, W, Be, Ta, Ag, and Re were reported as undetectable by all laboratories participating in the exercise.

Overall repeatability was assessed using average and median values of the relative standard deviations (RSDs) calculated from results of replicate preparations/analyses of individual sugar samples, typically on five replicates of each distributed sugar (Table 1). At first glance, these figures are not especially encouraging, as only a few elements show repeatability better than 10% RSD. However, this outcome is not unexpected, since, for many elements, concentrations were approaching LODs, at least for some of the techniques used. Generally, the trend is that the lower the instrumental LOD, the better the observed repeatability, as exemplified by corresponding figures from two data sets generated using ICP-SFMS (repeatability is better than 10% RSD for 17 elements reported by both laboratories). It seems that instrumental limitations stemming from analyses at trace concentrations and the challenge of controlling preparation blanks, rather than sample inhomogeneity, are responsible for the relatively poor overall repeatability observed.

For any given analyte and individual sugar sample, the comparability of results was assessed as the RSD for mean concentrations obtained by different laboratories. The evaluations were performed only when at least three, independent, individual elemental concentration values were available, and included outlier rejection (3σ-test) as well as results with accompanying repeatability poorer than 50% RSD. The number of sugar samples with RSDs for accepted results below 30% (arbitrary criterion of acceptable comparability used in the study, Table 1) reflects overall quantification capabilities of the present program for any given element. For 39 elements, acceptable comparability was obtained in at least one sugar sample, while results for 21 elements fulfilled the criteria for more than nine sugars.

Data for Rb show closest agreement (the highest score of 15), followed by P and, rather surprisingly, Zr. For many analytes, systematic instrument-specific bias can be revealed, as illustrated in Fig. 2 using Cr and Rb data as examples for four refined beet and four raw cane samples. Two laboratories using ICP-QMS reported almost identical Cr concentrations of approximately 200 ng g<sup>-1</sup> for all eight sugar samples that are consistently higher (by factors 10–200) than four sets of ICP-SFMS data (Fig. 2a). Most probably this discrepancy is caused by improper correction for spectral interferences originating from the sugar matrix (see Fig. 1 and Taylor et al., 2005). For Rb – an element relatively unaffected by spectral interferences in ICP-MS – the agreement between ICP-QMS and ICP-SFMS results is much closer (Fig. 2b). Data from ICP-



**Fig. 1.** Examples of spectral interferences in the vicinities of  $^{27}\text{Al}$  (a,  $m/z = 26.9815$ ),  $^{28}\text{Si}$  (b,  $m/z = 27.9769$ ),  $^{31}\text{P}$  (c,  $m/z = 30.9738$ ),  $^{44}\text{Ca}$  (d,  $m/z = 43.9555$ ),  $^{52}\text{Cr}$  (e,  $m/z = 51.9405$ ),  $^{53}\text{Cr}$  (f,  $m/z = 52.9407$ ),  $^{60}\text{Ni}$  (g,  $m/z = 59.9308$ ) and  $^{62}\text{Ni}$  (h,  $m/z = 61.9283$ ).

OES compare well with other techniques for cane samples (Rb concentrations above  $400 \text{ ng g}^{-1}$ ), while they are significantly positively biased for beet sugars (at approximately 20-fold lower level), indicating difficulties with blank subtraction at concentrations approaching the LOD.

Mean concentrations obtained for IAEA-C6 and Ultrex sucrose, as well as ranges for 12 sugar samples, are given in Table 2. The certificate of analysis for Ultrex Sucrose contains information on a broad range of non-metallic and metallic impurities, unfortunately given as below the corresponding LODs (as a rule in the  $\mu\text{g g}^{-1}$

range) for the majority of elements, while in general agreement with the findings of the present study, tabulated concentrations of B and Hg ( $200 \text{ ng g}^{-1}$  and  $0.3 \text{ ng g}^{-1}$ , respectively) are significantly higher than found in the present study. As an additional check for the consistency of our results, mean concentrations and measured ranges for beet and cane samples were compared with previously published data. It should be noted that the majority of data available in the literature refer to 'white' or refined sugar, often without further details on sugar type or origin. Nevertheless, there is broad agreement between previously published values and the



**Table 1**  
Summary of figures of merit.

	LOD, ng g <sup>-1</sup> , lowest reported	Number of submitted data sets (complete data sets)	Overall repeatability Mean (median), %	Repeatability for ICP-SFMS, %		Number of sugar samples with comparability better than 30%
				Lab. A	Lab. B	
K	700	9(8)	9(4)	4	5	12
Ca	50	9(6)	16(6)	4	2	12
S	300	3(2)	13(7)	5	2	7
Mg	2	9(6)	23(10)	4	7	8
Na	5	9(7)	18(8)	7	9	6
Si	300	3(0)	14(8)	10	9	7
P	5	3(2)	15(13)	11	15	14
Fe	3	9(6)	19(14)	12	5	9
Al	2	8(3)	24(17)	6	4	5
Mn	0.2	8(5)	16(7)	5	12	11
Sn	0.2	8(5)	30(21)	22	21	8
Cu	0.4	8(5)	15(8)	6	7	11
Sr	0.3	9(5)	16(7)	5	4	11
Rb	0.1	8(5)	8(5)	5	6	15
Br	20	2(0)	36(35)	18	33	0
Zn	2	8(5)	23(15)	13	11	12
Ti	0.2	6(4)	33(26)	15	7	10
Ba	0.08	8(5)	31(17)	5	8	9
B	2	3(0)	18(11)	8	16	1
Se	5	4(0)	45(22)	12	16	1
Ni	0.1	6(4)	21(14)	7	6	9
V	0.1	6(5)	13(10)	7	3	6
As	0.5	3(0)	39(24)	18	22	0
Cr	0.09	7(6)	18(10)	15	8	7
Co	0.04	7(4)	22(11)	9	14	8
Mo	0.02	3(3)	19(11)	6	12	9
Cs	0.01	6(4)	23(9)	4	9	10
I	5	2(0)	47(19)	15	40	0
Pb	0.05	7(4)	38(27)	8	12	9
Li	0.2	4(0)	19(12)	11	10	3
Zr	0.02	4(3)	15(12)	13	10	14
Cd	0.01	3(2)	28(16)	15	10	11
Y	0.01	4(0)	34(26)	11	11	8
Tl	0.005	4(3)	25(19)	5	5	11
Ga	0.05	3(0)	29(23)	20	40	0
Sc	0.01	3(0)	45(39)	18	11	0
Sb	0.02	3(3)	36(9)	16	7	13
La	0.004	4(0)	37(15)	9	19	1
Ce	0.009	4(0)	67(43)	15	21	4
Pr	0.002	3(0)	74(21)	20	18	0
Nd	0.004	3(0)	38(20)	12	8	0
Sm	0.002	3(0)	49(27)	17	24	0
Eu	0.005	3(0)	48(26)	13	40	0
Gd	0.002	3(0)	46(23)	21	20	0
Tb	0.002	3(0)	44(24)	13	22	0
Dy	0.004	3(0)	54(36)	10	14	0
Ho	0.001	3(0)	72(50)	10	23	0
Er	0.002	3(0)	61(47)	16	44	0
Tm	0.001	3(0)	67(34)	18	54	0
Yb	0.002	3(0)	75(51)	12	40	0
Lu	0.001	3(0)	80(51)	29	18	0
Te	0.03	4(0)	85(74)	32	130	0
U	0.001	4(2)	51(13)	9	6	8
Th	0.0005	4(0)	49(36)	11	11	6
Nb	0.01	3(0)	49(29)	22	20	0
Hg	0.02	4(0)	60(51)	24	35	4
W	0.01	3(0)	51(28)	8	7	0
Bi	0.004	4(2)	40(29)	12	14	13
Hf	0.002	3(2)	24(16)	14	7	11
Be	0.01	3(0)	79(43)	35	28	0
Ta	0.01	3(0)	75(51)	34	74	0
Ag	0.01	3(0)	53(39)	30	49	0
Re	0.0005	3(0)	83(69)	34	32	0

ranges found for refined beet sugars analyzed during this program. One notable exception is the significantly higher Ag level reported by Mohamed (1999) for Egyptian cane sugar (analysis by INAA). The Au level of 5 ng g<sup>-1</sup> found by Mohamed (1999) also seems to be very elevated. In the present suite of sugars, the Au content was consistently below 1 pg g<sup>-1</sup>, i.e., at least 5000 times lower.

Raw cane sugar samples contained, on average, 40 times higher levels of inorganic impurities than refined beet sugar samples. Consequently, multi-element analyses of the former sugars present relatively little challenge for sensitive ICP-MS techniques. However, the corresponding differences for B, Pb, Cd, U and Re were significantly lower indicating the introduction

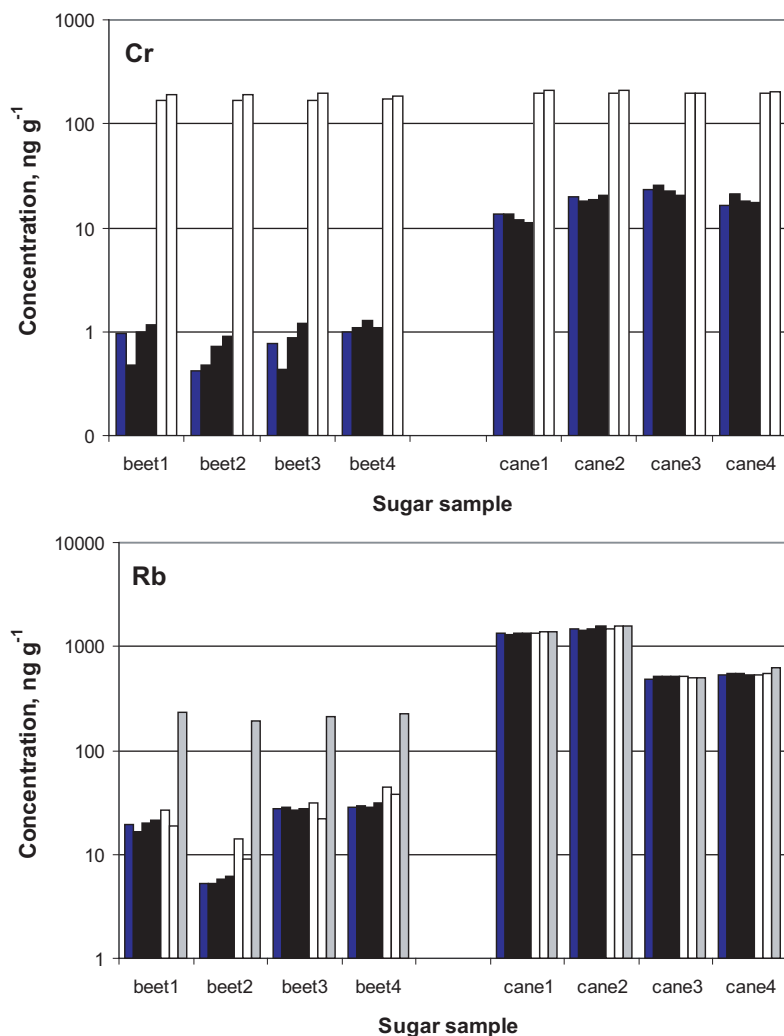


Fig. 2. Results obtained by different techniques (ICP-SFMS—black filled bars, ICP-QMS—open bars, ICP-OES—grey-filled bars) for Cr and Rb in beet and cane sugars.

of contamination sources at post-refinement stages. The ranges of observed concentrations were significantly wider for refined beet sugars, with maximum to minimum concentration ratios greater than 50 for Ca, Mg, Mn, Sr, Ba, Co, Mo, Pb, Cd and U. In comparison, the corresponding ratios are below 10 for the majority of elements in cane sugars, and were above 20 only for Se, Co and Li.

Differences in elemental concentrations between cane and beet sugars are likely due to several factors. Variations in impurities originating from processing and packaging may be partially responsible. However, concentration differences mostly appear to be due to the degree of refinement of the samples. As mentioned above, beet sugar samples, commercially classified as refined beet sugar, were in the form of fine, white crystals of highly purified sucrose, while cane sugar samples, commercially classified as raw cane sugar, were in the form of coarse, brown crystals made up of sucrose and containing both biological and mineral plant residue. This residue, removed during the refinement process, appears to be the cause of the elevated levels of elements in raw cane sugar, as suggested by the following evidence. Based on their  $\delta^{13}\text{C}$  values, the IAEA C6 and Ultrex sucrose samples were of cane sugar origin. However, their physical appearance indicated they were processed to a degree of refinement similar to the beet sugar samples. In addition, their element concentrations were of the same orders of magnitude as those found in the beet sugar samples. And finally, statistical testing showed that they clustered with the beet sugar samples.

Thus, it appears that removal of the plant residue present in raw sugar results in low levels of elements in refined sugar samples, whether of cane or beet origin.

#### 4.3. Isotope ratios

A summary of Pb, Sr and C isotope ratio data reported for the sugar samples is presented in Table 3. Two laboratories using ICP-SFMS measured lead isotope ratios in the solutions remaining after multi-element analyses. Mean repeatability varied from 0.2% RSD for the  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio to 1.3% for the  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio. Mean bias between the two sets of data was below 0.7%, with correlation coefficients ( $R^2$ ) in the range 0.81–0.95. It seems that, despite better repeatability being observed for the  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio, the wider range of ratios measured in sugars from this study (7.5% relative) and the best between-laboratory correlation ( $R^2 = 0.95$ ) make the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio especially promising for studies focused on provenance determination. Though better repeatability and lower bias between different laboratories has been reported for lead isotope ratio measurements by ICP-MS previously (i.e., Hinners et al., 1998), the results obtained here must be considered acceptable considering that all analyses were performed using solutions containing below  $1 \text{ ng g}^{-1}$  Pb. The low incipient Pb contents of sugars may also limit the usefulness of the potentially much more precise technologies of TIMS and MC-ICP-MS, unless extensive analyte pre-concentration/matrix separation routines are incorporated into sample preparation.

**Table 2**  
Element concentrations in sugars.

	Unit	IAEA-C6 (SD)	Ultrex grade sucrose (SD)	Refined beet sugars (SD) (n=8)	Unprocessed cane sugars (SD) (n=4)	Published data (NA—data not available)
K	μg g <sup>-1</sup>	11.0(0.7)	7.3(0.6)	25(4–38)	600(250–1100)	34.5 <sup>a</sup>
Ca	μg g <sup>-1</sup>	1.3(0.2)	0.86(0.50)	6.8(0.05–29)	230(100–500)	1450 <sup>a</sup>
S	μg g <sup>-1</sup>	0.43(0.23)	0.42(0.13)	3.6(0.3–6.0)	130(50–300)	NA
Mg	μg g <sup>-1</sup>	0.25(0.06)	0.08(0.01)	0.08(0.005–0.39)	76(40–110)	1.01 <sup>a</sup>
Na	μg g <sup>-1</sup>	1.3(0.2)	1.8(0.1)	6.4(0.6–18)	25(4–60)	1.6 <sup>a</sup>
Si	μg g <sup>-1</sup>	0.48(0.06)	<0.3	0.8(<0.3–2.1)	41(20–75)	NA
P	μg g <sup>-1</sup>	0.10(0.02)	0.046(0.009)	0.8(0.1–3.0)	27(18–42)	NA
Fe	μg g <sup>-1</sup>	0.12(0.02)	0.076(0.049)	0.08(0.02–0.25)	11(4–25)	0.23 <sup>a</sup>
Al	μg g <sup>-1</sup>	0.024(0.011)	0.027(0.009)	0.06(0.006–0.24)	2.2(0.4–2.0)	0.9–2.4 <sup>b</sup>
Mn	ng g <sup>-1</sup>	2.2(0.7)	1.0(0.8)	25(0.2–83)	1100(400–2000)	7–15 <sup>c</sup> , 2–10 <sup>b</sup> , 15 <sup>a</sup>
Sn	ng g <sup>-1</sup>	3.3(1.5)	1.6(0.5)	1.5(0.3–4)	510(130–2000)	NA
Cu	ng g <sup>-1</sup>	19(2)	42(4)	33(4–78)	520(100–1200)	99–570 <sup>c</sup> , 70–300 <sup>b</sup> , 18 <sup>a</sup> , 16–47 <sup>d</sup>
Sr	ng g <sup>-1</sup>	11(6)	4.3(1.8)	24(0.4–160)	650(190–1400)	25 <sup>a</sup>
Rb	ng g <sup>-1</sup>	20(2)	5.9(1.8)	22(3–30)	920(400–1500)	NA
Br	ng g <sup>-1</sup>	<20	<20	<20	400(140–800)	NA
Zn	ng g <sup>-1</sup>	24(3)	4.7(0.2)	29(2–80)	340(170–620)	24–100 <sup>c</sup> , 0.4–200 <sup>b</sup> , 4 <sup>a</sup> , 13–79 <sup>d</sup>
Ti	ng g <sup>-1</sup>	1.0(0.3)	0.49(0.05)	7(0.5–22)	140(20–400)	NA
Ba	ng g <sup>-1</sup>	19(1)	1.2(0.3)	3(0.1–20)	190(50–300)	NA
B	ng g <sup>-1</sup>	<2	<2	110(10–400)	70(40–120)	NA
Se	ng g <sup>-1</sup>	<5	<5	<5	29(<5–100)	NA
Ni	ng g <sup>-1</sup>	0.9(0.4)	0.5(0.4)	1.7(0.1–4.5)	31(8–60)	<0.2 <sup>b</sup> , 7 <sup>a</sup>
V	ng g <sup>-1</sup>	0.7(0.3)	0.7(0.3)	0.5(0.1–0.8)	21(4–60)	NA
As	ng g <sup>-1</sup>	0.5(0.3)	0.8(0.6)	0.6(<0.5–0.9)	19(8–50)	<2–11 <sup>d</sup>
Cr	ng g <sup>-1</sup>	0.9(0.3)	0.6(0.2)	0.5(0.2–1.1)	18(10–30)	<4–20 <sup>c</sup> , 3.5–6.5 <sup>b</sup> , 10 <sup>a</sup>
Co	ng g <sup>-1</sup>	0.16(0.09)	0.14(0.10)	0.7(0.04–3.3)	16(1–25)	11 <sup>a</sup>
Mo	ng g <sup>-1</sup>	0.42(0.12)	0.97(0.22)	0.28(0.02–0.80)	14(3–30)	NA
Cs	ng g <sup>-1</sup>	0.12(0.03)	0.09(0.06)	0.06(0.01–0.14)	4.6(5–10)	NA
I	ng g <sup>-1</sup>	<5	<5	<5	14(<5–20)	NA
Pb	ng g <sup>-1</sup>	90(8)	0.71(0.02)	4(0.06–30)	29(9–100)	<5–10 <sup>c</sup> , 2.7–5.4 <sup>b</sup> , 8 <sup>a</sup> , <5 <sup>e</sup> , <2–34 <sup>d</sup>
Li	ng g <sup>-1</sup>	<0.2	<0.2	0.6(<0.2–2.7)	7(1–22)	NA
Zr	ng g <sup>-1</sup>	0.06(0.02)	0.05(0.01)	0.38(0.07–1.3)	3(1–7)	NA
Cd	ng g <sup>-1</sup>	0.39(0.04)	0.036(0.006)	0.86(0.01–4.8)	1.0(0.3–2.0)	<1–2 <sup>c</sup> , 0.3–9 <sup>b</sup> , 1 <sup>e</sup> , <2–10 <sup>d</sup>
Y	ng g <sup>-1</sup>	0.019(0.002)	<0.01	0.018(<0.01–0.10)	1.5(0.3–3.0)	NA
Tl	ng g <sup>-1</sup>	0.027(0.020)	0.008(0.001)	0.09(0.01–0.28)	1.3(0.2–3.3)	NA
Ga	ng g <sup>-1</sup>	0.09(0.03)	<0.05	0.05(<0.05–0.10)	0.7(0.2–1.6)	NA
Sc	ng g <sup>-1</sup>	0.010(0.006)	0.011(0.007)	0.009(<0.01–0.019)	0.5(0.1–1.3)	NA
Sb	ng g <sup>-1</sup>	0.65(0.08)	0.38(0.15)	1.9(0.3–2.2)	1.3(0.4–3.0)	NA
La	pg g <sup>-1</sup>	39(22)	42(35)	10(<4–50)	1500(400–3600)	NA
Ce	pg g <sup>-1</sup>	37(18)	14(11)	21(<9–80)	3300(800–8400)	NA
Pr	pg g <sup>-1</sup>	20(15)	30(20)	4(<2–11)	400(110–1000)	NA
Nd	pg g <sup>-1</sup>	18(6)	14(11)	8(<4–38)	1500(400–3900)	NA
Sm	pg g <sup>-1</sup>	13(10)	18(15)	4(<2–11)	330(90–800)	NA
Eu	pg g <sup>-1</sup>	<5	<5	<5	80(20–180)	NA
Gd	pg g <sup>-1</sup>	<2	<2	<2	340(70–900)	NA
Tb	pg g <sup>-1</sup>	<2	<2	<2	46(11–100)	NA
Dy	pg g <sup>-1</sup>	<4	<4	<4	260(50–560)	NA
Ho	pg g <sup>-1</sup>	<1	<1	<1	50(10–100)	NA
Er	pg g <sup>-1</sup>	<2	<2	<2	140(30–280)	NA
Tm	pg g <sup>-1</sup>	<1	<1	<1	20(4–40)	NA
Yb	pg g <sup>-1</sup>	<2	<2	<2	120(30–250)	NA
Lu	pg g <sup>-1</sup>	<1	<1	<1	20(6–40)	NA
Te	pg g <sup>-1</sup>	<30	<30	<30	400(<30–600)	NA
U	pg g <sup>-1</sup>	8(2)	3(2)	100(5–400)	510(90–1600)	<100 <sup>b</sup>
Th	pg g <sup>-1</sup>	0.8(0.1)	0.7(0.2)	3(<0.5–10)	270(80–720)	NA
Nb	pg g <sup>-1</sup>	14(7)	13(9)	<10	390(100–1100)	NA
Hg	pg g <sup>-1</sup>	55(7)	75(23)	<20	170(50–360)	NA
W	pg g <sup>-1</sup>	153(13)	<10	<10	310(80–1200)	NA
Bi	pg g <sup>-1</sup>	29(11)	7(3)	7(4–22)	170(60–500)	NA
Hf	pg g <sup>-1</sup>	5(3)	6(4)	21(4–49)	170(50–390)	NA
Be	pg g <sup>-1</sup>	<10	<10	<10	80(12–250)	NA
Ta	pg g <sup>-1</sup>	20(3)	28(9)	<10	23(<10–60)	NA
Ag	pg g <sup>-1</sup>	26(11)	35(19)	20(<10–40)	70(30–190)	2000 <sup>a</sup>
Re	pg g <sup>-1</sup>	<0.5	<0.5	1.3(<0.5–5.6)	1.8(<0.5–4.0)	NA

<sup>a</sup> Mohamed (1999).<sup>b</sup> Santos et al. (2004).<sup>c</sup> Jorhem and Sundström (1993).<sup>d</sup> Sancho et al. (1997, 1998, 2000).<sup>e</sup> Fecher and Ruhnke (2002).

**Table 3**  
Compilation of isotope ratio data for sugars.

Pb						
Technique	ICP-SFMS		Number of laboratories: 2	Number of samples: 9		
	Mean (SD)	Range		Mean repeatability RSD (range), %	Mean bias <sup>a</sup> (range), %	R <sup>2</sup>
<sup>206</sup> Pb/ <sup>204</sup> Pb	18.25(0.50)	17.45–18.95		1.3(0.4–6.0)	0.7(0.08–1.6)	0.81
<sup>207</sup> Pb/ <sup>206</sup> Pb	0.8535(0.0183)	0.8303–0.8925		0.4(0.04–0.7)	0.3(0.04–0.5)	0.95
<sup>208</sup> Pb/ <sup>207</sup> Pb	2.440(0.019)	2.397–2.463		0.2(0.07–0.5)	0.15(0.03–0.3)	0.88
Sr						
Technique	TIMS, ICP-SFMS, MC-ICP-MS		Number of laboratories: 3	Number of samples: 3		
		Mean (SD)	ICP-SFMS	MC-ICP-MS	Mean (SD)	
Sugar A		0.70845(0.00004)	0.7081(0.0003)		0.70847(0.00002)	
Sugar B		0.71024(0.00005)	0.7103(0.0003)		0.70996(0.00003)	
Sugar C		0.70978(0.00020)	0.7090(0.0004)		0.70966(0.00009)	
Mean RSD (range), %		0.013(0.005–0.028)	0.047(0.04–0.06)		0.006(0.002–0.013)	
			R <sup>2</sup>		Mean bias <sup>a</sup> (range), %	
		TIMS vs. ICP-SFMS	0.88		0.037(0.0008–0.074)	
		TIMS vs. MC-ICP-MS	1.00		0.014(0.0013–0.028)	
		MC-ICP-MS vs. ICP-SFMS	0.84		0.043(0.029–0.062)	
Sr						
Technique	IRMS		Number of laboratories: 2	Number of samples: 14		
	Mean (SD)	Range		Mean repeatability RSD (range), %	Mean bias <sup>a</sup> (range), %	R <sup>2</sup>
δ <sup>13</sup> C cane <sup>b</sup> , ‰	–11.70(0.52)	(–10.5–12.6)		0.13(0.01–0.7)	0.19(0.16–0.20)	1.00
δ <sup>13</sup> C beet, ‰	–24.98(0.75)	(–23.8–26.5)		0.19(0.1–0.9)		

<sup>a</sup> Bias between results obtained by different analytical techniques.

<sup>b</sup> Cane sugars include IAEA-C6 and Ultrex sucrose.

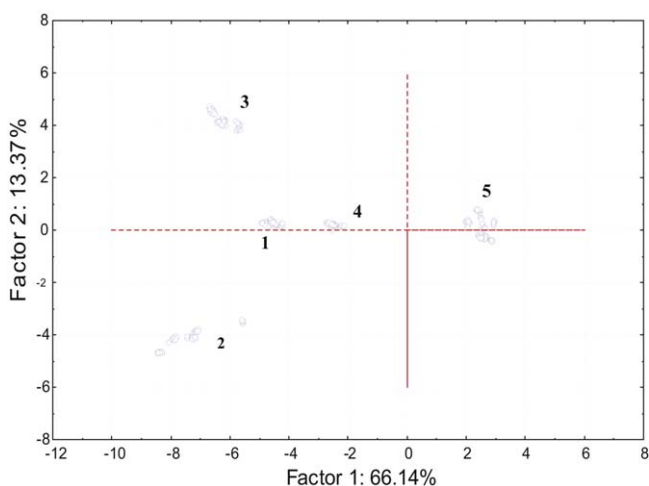
Owing to the limited sample size available, Sr isotope ratios were measured in only three cane sugar samples with high Sr contents. Among the three techniques used, ICP-SFMS, MC-ICP-MS and TIMS, the first-mentioned is least precise, while the mean repeatability of the latter two is better than 0.01%. In spite of differences in precision, all three techniques were suitable for the purpose of differentiating sugar samples on the basis of Sr isotope ratios. Comparability is best for TIMS and MC-ICP-MS, with an average bias of only 0.014% (Table 3).

Two laboratories measured <sup>13</sup>C using IRMS. Values for δ<sup>13</sup>C fell into two groups, around –12‰ for cane sugars and –25‰ for beet sugars. Mean repeatability values were 0.13% RSD for cane sugar samples and 0.19% for beet sugar samples. Mean bias between the

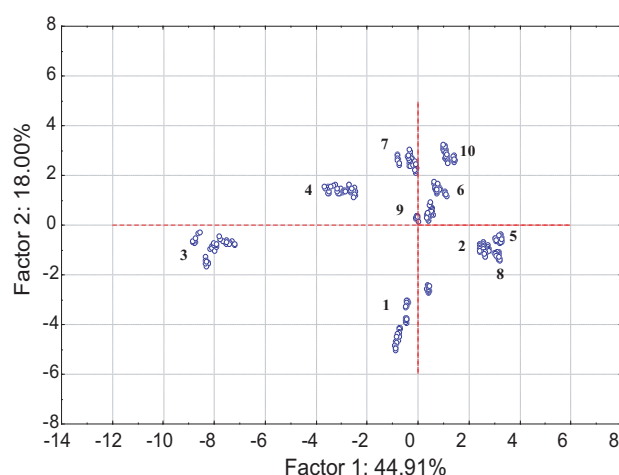
two sets of data was 0.19%, with a correlation coefficient (R<sup>2</sup>) of 1.00, indicating excellent agreement between the two laboratories, as would be expected for this well established technique. Based on this limited set of samples, it appears cane and beet sugars can be clearly differentiated on the basis of their δ<sup>13</sup>C levels.

#### 4.4. Geographic origin

An exploratory determination of geographic origin was investigated using principal components analysis (PCA) to observe possible groupings present in the dataset. Concentrations of 22 trace elements (Al, B, Ba, Ca, Co, Cr, Cs, Cu, Fe, Li, K, Mg, Mn, Na, Ni, Pb, Rb, Sn, Sr, Ti, V and Zn) were used to examine whether 14 sugar



**Fig. 3.** Results of PCA using 22 elements and 14 sugar samples. Groups 1–4 represent 4 raw cane sugar samples from 4 different geographic locations, Louisiana, USA (1), Costa Rica (2), Argentina (3) and Swaziland (4). Group 5 represents 10 refined sugar samples: IAEA-C6, Ultrex sucrose and 8 beet sugar samples from 8 different geographic locations; see Fig. 4 for locations. Factor 1 was most highly correlated with Al, Ca, Cr, Cu, Fe, Ni, and V; factor 2 was most highly correlated with Cs, Pb, and Zn.



**Fig. 4.** Results of PCA using 22 elements and 10 refined sugar samples (raw cane sugars excluded). Group 1 represents the IAEA-C6 sample (cane origin). Group 2 represents the Ultrex sucrose (cane origin). Groups 3–10 represent 8 refined beet sugar samples from 8 different geographic locations, Moldova (3), Poland (4), Idaho, USA (5), Netherlands (6), France (7), Germany (8), Hungary (9) and Michigan, USA (10). Factor 1 was most highly correlated with Al, Ca, Cs, Fe, Mn and Ni; factor 2 was most highly correlated with Ba, K, Mg, Na and Pb.



samples (6 cane and 8 beet) were distinguishable from one another (based on  $\delta^{13}\text{C}$  measurements, the Ultrex sucrose and IAEA-C6 samples were derived from cane sugar). These elements were selected to minimize the number of missing values and below-LOD measurements in the dataset. As shown in Fig. 3, the four raw cane sugar samples (Groups 1–4) were clearly distinguishable from each other and from the fifth group, which contained the eight refined beet sugar samples, as well as the IAEA-C6 and Ultrex samples. Good separation between the groups is due to relatively large differences in concentration between sample types and locations. In contrast, when the 10 refined samples were examined separately (Fig. 4), distinct sample groupings were found, but not all were well separated. This is due to much smaller differences in concentration between the refined samples, whether of cane or beet origin. Although the statistical significance of the separations was not noted, greater numbers of measurements and better measurement precision would increase the likelihood of differentiating groups.

## 5. Conclusions

Concentrations of 63 elements, as well as carbon, lead and strontium isotopes, were measured in samples of cane and beet sugar from different geographic origins. Simple dissolution in 0.14 M  $\text{HNO}_3$  was sufficient to produce solutions suitable for multi-element analysis by various ICP-based techniques. Measuring many of the least-detectable elements required the enhanced sensitivity of ICP-SFMS. Raw sugars contained much higher levels of most elements than refined sugars, whether of cane or beet origin.  $\delta^{13}\text{C}$  levels can be used to clearly distinguish between pure samples of beet and cane sugars. Determining the geographic origin of sugars appears feasible using elemental fingerprinting.

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