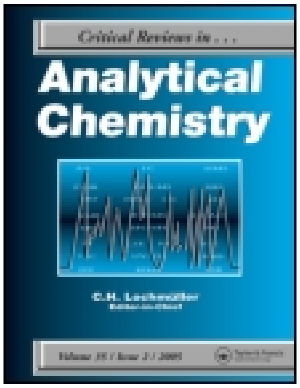

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Elemental Composition of White Refined Sugar by Instrumental Methods of Analysis

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This overview deals with an important issue for the sugar industry, the elemental analysis of white refined sugar by atomic absorption spectrometry and other instrumental methods, including inductively coupled plasma optical emission spectrometry, neutron activation analysis, and stripping voltammetry. Strong and weak points of these methods in terms of determinations of major and trace elements in sugar samples are featured. Different sample preparation procedures applied in sugar analysis, with their advantages and disadvantages, are discussed. The importance of quality assurance and control of results are highlighted. Separate sections are focused on sources of elements in white refined sugar and various food safety and technological aspects related to their presence.

Keywords White sugar, sample preparation, analysis, trace elements, instrumental methods

SOURCE OF ELEMENTS IN SUGAR AND NECESSITY OF THEIR DETERMINATION

White refined sugar is sucrose of a very high purity (>99.9%) that is industrially produced from sugar beet or cane and commonly used for baking, cooking, and sweetening domestic food products and beverages or technologically applied to prepare other processed food and beverages (Miller-Ihli, 1995; Skrbic and Gyura, 2007; Skrbic et al., 2010). Unfortunately, in large-scale sugar processing and refining, a great number of chemicals, including $Ca(OH)_2$ and CaO (lime), H_2SO_4, H_3PO_4, bleaching and flotation reagents, and de-colorants of different purity and quality used at different subsequent production steps are usually responsible for contamination of white refined sugar by- and end products (Skrbic and Gyura, 2006, 2007; Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Mohamed, 1999; Waheed et al., 2009). Refined beet or cane sugar may typically contain some significant amounts of soluble and/or insoluble organic and inorganic impurities that change, on the whole, its quality and market value (Skrbic et al., 2010; Wojtczak and Krol, 2002; Wojtczak, 2006). The contribution of water-insoluble matter in sugar is quite high and is typically affected by local conditions of the technological processes, i.e., aids and additives (Wojtczak, 2006). Main elements of this insoluble matter are Ca and Fe (about 30% on the whole), which are present as $CaCO_3$ and Fe_2O_3, respectively (Ronda et al., 2001). The remaining 70% of the insoluble matter is presumed to be composed of some organic impurities and/or silicates (Ronda et al., 2001).

Depending on the content of inorganic (mineral) impurities, i.e., major (Ca, K, Mg) and trace elements (As, Cd, Cu, Fe, Mn, Hg, Pb, Zn), white refined sugar can contribute nutritional value to the daily diet of infants and adults (Skrbic et al., 2003, 2010; Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Ronda et al., 2001; Sancho et al., 1997, 1998). Indeed, the presence of Ca, K, and Mg as well as Co, Cr, Fe, and Mn seems to be a dietary essential (Mohamed et al., 1989). However, levels of these elements in white refined sugar are low, and, hence, average daily intakes of elements from sugar, added to sweeten consumed beverages and food products, are small compared to that of other food products (Skrbic and Gyura, 2007).

The type and content of trace elements in white refined sugar directly depends on the quality of the sugar beet and cane from which sucrose is isolated, and, correspondingly, this is related to a great extent to soil mineralization and kinds of fertilizers and irrigation used during plant cultivation (Skrbic and Gyura, 2007; Sancho et al., 1998; Skrbic et al., 2003; Mohamed et al., 1989; Awadallah et al., 1985; De Bruijn and Bout, 1999). The nature and characteristics of the arable land, including structure and composition of soil on which both sugar-rich plants are grown, and the degree of its pollution also matter (Skrbic and

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Gyura, 2007; Mohamed, 1999; Sancho et al., 1998; Skrbic et al., 2003). Concentrations of most elements (Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Sr, and Zn) are much higher in crude juices than in sugar (Mohamed, 1999). The content of these elements at subsequent stages of sugar production tends to gradually decrease and usually reaches minimum values in the final product (Mohamed, 1999; Awadallah et al., 1984, 1985, 1986, 1995). This proves that plants and soils are the most important sources of elements of primary origin in white refined sugar (Skrbic et al., 2010; Awadallah et al., 1995). However, due to individual sugar production technology and process conditions used in different companies and mills, some elements, like K, Na, Mg, Mn, Zn, may not change their concentrations during handling and processing when considering their concentrations in respective juices and sugar (Awadallah et al., 1995).

Handling and processing practices in a sugar mill completed in a given production line, i.e., extraction, liming, carbonation, filtration, evaporation, have an impact on the quality of sugar because they can be another source of elements in sugar (Skrbic and Gyura, 2007; Skrbic et al., 2003, 2010; Sancho et al., 1998; De Bruijn and Bout, 1999). Various aids and additives used at successive stages of sugar production as well as corrosion occurring in production tubing and machinery, additionally enhanced by passing CO_2 and SO_2, can contribute some trace elements to white refined sugar (Mohamed et al., 1989) (see Fig. 1 with subsequent steps of sugar production and possible sources of contamination with elements).

Accordingly, there is a group of elements (As, Co, Fe, Mn, Na, Ni, Pb, Sn, Zn, V) whose concentrations found in successive stage sugar products can be higher than those in juice (Mohamed, 1999; Awadallah et al., 1995). The content of these elements usually increases rapidly at the first stage of sugar production and remains nearly constant or gets higher at further steps, but finally, concentrations of these elements in sugar are almost the same as in juice (Mohamed, 1999; Awadallah et al., 1995). This reveals that the origin of elements in sugar is not environmentally related but results from juice concentration and applied treatment processes like additives, i.e., $Ca(OH)_2$, $Ca(H_2PO_4)_2$, and $Mg(OH)_2$, passage of CO_2 and SO_2, evaporation, and corrosion of machinery (boilers, containers) and lines that take place under local sugar production conditions (Mohamed, 1999; De Bruijn and Bout, 1999). Carbonation and subsequent filtration and purification processes are usually responsible for a general decrease of Ca and Mg surplus and trace elements in the final product (Mohamed, 1999; De Bruijn and Bout, 1999). Low concentrations of Ca and other elements in white refined sugar confirm the effectiveness of these production stages (De Bruijn and Bout, 1999).

Trace elements such As, Cd, Hg, and Pb are regarded as toxic and usually most of the concern in sugar industry is about these elements. In terms of dietary safety, it is obligatory to reliably ensure a proper quality of sugar, i.e., that it does not contain toxic elements or that these elements are present at concentrations lower than levels allowable by legislation (Skrbic et al., 2010; Sancho et al., 2001). The content of As, Cd, Hg, and Pb in white refined sugar is low and recognized to be uncritical. Concentrations of these elements lower than 5 ng g^{-1} typically do not pose any health hazard or produce any safety consequences or clinical concerns (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2010; Wojtczak and Krol, 2002). Indeed, As, Cd, Hg, and Pb contaminants in sugar do not significantly contribute to ingestion of these elements in a daily diet. An average weekly consumption of 100 g of white refined sugar can contribute from 0.4% (As) to 1.3% (Pb) of the weekly Recommended Dietary Allowances (RDAs) or Estimated Safe and Adequate Dietary Intakes (ESADIs) for these elements (Waheed et al., 2009). This is fairly low and harmless to health from a nutritional safety point of view.

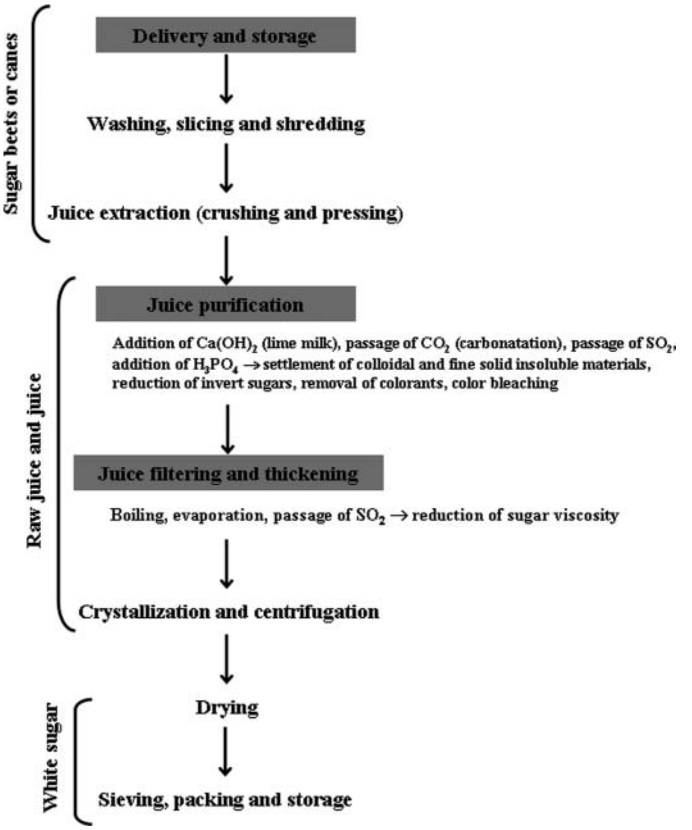

FIG. 1. Sugar production process and stages of potential contamination risk with elements (marked in grey) due to additives and corrosion of line and machinery (adopted from Awadallah et al., 1984, 1986, 1995).

Such a state of matters is probably the reason that European Union legislation with regulations adopted for maximum permitted levels for Cd, Hg, and Pb in foodstuffs does not include sugar at all (European Commission, 2001, 2005). This issue is usually regulated by national legislation and maximum acceptable limits for As, Cd, Cu, Pb, Hg, and Zn in white refined sugar and other related products are set to be within 10^{-1}–10^{0} μg g^{-1} (Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Sancho et al., 1997). Allowable concentrations of these metals are also specified by other international institutions devoted to settling standards for various foodstuffs, i.e., Codex Alimentarius Commission of Joint Food and Agriculture Organization and World Health Organization (Food and Agriculture Organization of the United Nations, World Health Organization, 1999).

In contrast, levels of Fe, Cu, and Zn, elements both of primary (related to sugar beet or cane plants and characteristics of soil in which they are grown) and secondary (associated with contamination and sugar processing) origins in white refined sugar, show a great variation. Information on concentrations of these elements is important from the view of technological process of sugar production (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Waheed et al., 2009; Dias and Cardoso, 2006). Accordingly, contents of these elements can be considered for assessing quality of by- and end sugar products and as an additional criterion for evaluating effectiveness of sugar refining, namely purification and filtration of juice or sugar crystallization and separation from molasses (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2010; Wojtczak and Krol, 2002). In this way, routine analyses of sugar for the content of trace elements are the legal duty of the sugar industry carried out to provide the best quality and safety of the final product prepared for commerce. Additionally, information on the kind and content of trace elements is a decisive factor for food manufacturers and other sugar customers (Ronda et al., 2001). Considering that white refined sugar is used in food manufacturing and processing to sweeten and/or supplement different beverages and food products, its quality regarding the control of concentrations of trace metals and suitability for certain technological and industrial applications are increasingly important aspects (Wojtczak and Krol, 2002; Wojtczak, 2006; Ronda et al., 2001).

For all reasons stated above, it is evident that controlling and monitoring elements in white refined sugar and related products from different sugar production stages are of particular interest and importance for the sugar industry (Wojtczak and Krol, 2002; Sancho et al., 1997). This implies suitable instrumental methods of analysis, which are critical in terms of reliable and dependable determinations of low and very low (trace and ultratrace) concentrations of nutrient and toxic elements.

PRESENCE OF CERTAIN ELEMENTS IN SUGAR AND THEIR IMPLICATIONS

Analysis of commercial sugar reveals that, except for Ca, K, Mg, and Na, it contains very low quantities of other elements, including As, Cd, Cr, Cu, Fe, and others (see collation in Tables 1 and 2 for sugar from different countries). Calcium in white refined sugar predominantly originates from beet processing during juice purification, i.e., addition of lime milk (Skrbic et al., 2010; De Bruijn and Bout, 1999). Normally, Ca and Mg ions are eliminated by precipitating them as respective carbonates (carbonation with CO_2), sulfites, and sulfates (Skrbic et al., 2010). However, when this process is incomplete due to a improper alkalinity, relatively high concentrations of Ca still remain in the sugar, indicating low effectiveness of juice purification (Skrbic et al., 2010; De Bruijn and Bout, 1999).

Concentrations of trace elements in commercial white refined sugars typically pursue the following pattern: Fe $>>$ Cd $>$ Cu $\approx$ Ni $\approx$ Zn $\approx$ Mn $>$ As $\approx$ Co $\approx$ Pb $\approx$ Hg. In fact, Fe, Cu, Mn, and Zn are elements that have certain physiological and nutritional implications and they are commonly at much higher concentrations than those with increasing toxicity, i.e., As, Co, Hg, and Pb (Skrbic and Burisic-Mladenovic, 2005; Skrbic et al., 2003; Sancho et al., 2000). Quite often, the latter elements, and Cd, Cr, Ni, and Sn as well, have very low concentration levels (< 10 ng g^{-1}) or are present in sugar below achievable detection limits of the methods applied for its analysis (Ronda et al., 2001; De Bruijn and Bout, 1999).

Iron exhibits rather a high concentration variation in sugar samples. This is mostly attributed to differences in raw materials (sugar beet or cane) and industrial processing for sugar retrieving and refining, i.e., extraction, filtration, and purification (Skrbic and Burisic-Mladenovic, 2005; Skrbic and Gyura, 2006). Elevated quantities of Fe increase ash conductivity of sugar and worsen color of sugar solutions and crystals (Skrbic and Gyura, 2006, 2007; Mohamed, 1999). Surprisingly, the majority of this element (50–80% of the total content in sugar) is present in the form of insoluble species that may come from technological lines, for example as rust, and is responsible for lower quality of sugar (Miller-Ihli, 1995; Wojtczak and Krol, 2002; Wojtczak, 2006). The presence of higher levels of Fe can also be associated with the corrosive character (relatively low pH values) of beet and cane juices and the dissolving of this element from materials of processing lines and equipment (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2010; De Bruijn and Bout, 1999). This effect can additionally be enhanced by CO_2 and SO_2, which are applied in sugar refining technology correspondingly for carbonation and extraction and evaporation and crystallization processes. Under such conditions, juice acidity lowers greatly and tends to corrode machinery, tanks, and containers used in sugar production (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2010; Mohamed, 1999).

Similarly, Fe, Cu, and Zn also present high variability in concentrations in sugar (Wojtczak and Krol, 2002; Ronda et al., 2001). Insoluble species (50–83% of the total content in sugar) are the most predominant forms of Cu (Wojtczak and Krol, 2002). The presence of higher quantities of this element in sugar is associated with unfavorable darker color and a decrease of market quality (Mohamed, 1999). The contribution of insoluble forms of Zn to the total content of this element in sugar is the most differentiated among other elements; it can vary from 12% to even 75% of total Zn (Wojtczak and Krol, 2002). This indicates a critical influence of sugar production technology and local conditions, including line materials and additives used, on sugar quality and the content of Cu and Zn (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2010; Wojtczak

TABLE 1
Contents of Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, and Li in white refined sugar from different countries

	Concentration of elements, μg g^{-1}										
Country of origin	Al	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li
Brazil (Dias and Cardoso, 2006)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]
Czech Republic (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.07–0.30	0.17–0.45	—[a]	—[a]	—[a]
Egypt (Mohamed, 1999; Awadallah et al., 1984, 1985, 1986, 1995)	0.0060–0.0620	0.0001–0.0006	0.14–1.5[b]	0.0069–0.0248	—[a]	0.006–0.402	0.010–0.099	0.16–527	—[a]	33–20000	0.001–0.008
EU countries[c] (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.03–0.05	0.23–0.41	—[a]	—[a]	—[a]
Germany (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.01–0.05	0.04–0.12	—[a]	—[a]	—[a]
Hungary (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.06–0.10	0.34–0.46	—[a]	—[a]	—[a]
Italy (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.07–0.11	0.23–0.28	—[a]	—[a]	—[a]
Netherlands (Miller-Ihli, 1995; De Bruijn and Bout, 1999)	—[a]	—[a]	0.8–4.1	—[a]	ND	—[a]	0.14–0.23	0.01–0.04	—[a]	30.4–48.1	—[a]
Poland (Wojtczak and Krol, 2002, Wojtczak, 2006)	—[a]	—[a]	1.4–19.5	—[a]	—[a]	—[a]	0.01–0.36	0.– 1.13	—[a]	—[a]	—[a]
Serbia (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2003; 2010; Skrbic and Burisic-Mladenovic, 2005)	< 0.02	—[a]	13.65–15.07	0.030–0.160	—[a]	—[a]	0.005–0.120	0.09–54.65	< 0.001	16.01–20.21	—[a]
Slovakia (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.07–0.18	0.13–0.48	—[a]	—[a]	—[a]
Turkey (Leblebici and Volkan, 1998)	0.0041–0.089	—[a]	—[a]	—[a]	—[a]	—[a]	0.020–0.035	1.41–1.79	—[a]	—[a]	—[a]
Spain (Wojtczak and Krol, 2002; Ronda et al., 2001; Sancho et al., 1997, 1998, 2000, 2001; Mohamed et al., 1989; Carbonell-Barrachina et al., 2002)	ND-0.07	—[a]	—[a]	0.0004–0.010	< 0.001–0.008	0.0015–0.0053	0.016–1.4	0.20–0.59	ND-0.0012	—[a]	—[a]

[a] Data not available.

[b] b In % (m/m).

[c] Concerning Austria, France, and Greece.

ND: not detected.

TABLE 2
Contents of Mg, Mn, Na, Ni, P, Pb, Sc, Sn, Sr, V, and Zn in white refined sugar from different countries

	Concentration of elements, $\mu g\ g^{-1}$										
Country of origin	Mg	Mn	Na	Ni	P	Pb	Sc	Sn	Sr	V	Zn
Brazil (Dias and Cardoso, 2006)	—[a]	—[a]	—[a]	—[a]	—[a]	<0.01	—[a]	—[a]	—[a]	—[a]	—[a]
Czech Republic (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.03–0.06
Egypt (Mohamed, 1999; Awadallah et al., 1984, 1985, 1986, 1995)	0.96–2000	0.012–18.0	1.50–1100	0.0040–0.0100	4–70	0.0002–0.0120	0.0016–0.0023	0.0001–0.0024	0.0200–0.0300	0.0190–0.0450	0.004–0.131
EU countries[b] (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.03–0.04
Germany (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.01–0.08
Hungary (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.08–0.10
Italy (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.06–0.08
Netherlands (Miller-Ihli, 1995; De Bruijn and Bout, 1999)	0.1–0.3	ND–0.04	6.5–8.5	ND	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.02–0.06
Poland (Wojtczak and Krol, 2002, Wojtczak, 2006)	0.07–0.46	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.02–0.30
Serbia (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2003; 2010; Skrbic and Burisic-Mladenovic, 2005)	0.06–0.12	0.003–0.015	6.03–7.05	—[a]	—[a]	< 0.002–0.03	—[a]	—[a]	—[a]	—[a]	0.010–14.13
Slovakia (Wojtczak and Krol, 2002)	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	0.02–0.04
Turkey (Leblebici and Volkan, 1998)	—[a]	—[a]	—[a]	—[a]	—[a]	0.045–0.060	—[a]	—[a]	—[a]	—[a]	—[a]
Spain (Wojtczak and Krol, 2002; Ronda et al., 2001; Sancho et al., 1997, 1998, 2000, 2001; Mohamed et al., 1989; Carbonell-Barrachina et al., 2002)	—[a]	—[a]	—[a]	< 0.003–0.032	—[a]	< 0.002–0.034	—[a]	< 0.004–0.015	—[a]	—[a]	0.013–0.082

[a] Data not available.

[b] Concerning Austria, France, and Greece.

ND: not detected.

and Krol, 2002). However, differences in the content of Zn due to variance in processed beets and their quality seem to be much more profound than the effect of technological conditions (Skrbic and Gyura, 2006, 2007; De Bruijn and Bout, 1999). The same can be observed for Mn (De Bruijn and Bout, 1999). Variations in average concentrations of Fe, Cu, and Zn do not only exist in white refined sugar of different country origins. Local production conditions used in refineries and certain line materials and additives used in technological processes can be responsible for great differences in concentrations of Fe, Ca, and Zn even between refineries located in the same country or region (Skrbic and Gyura, 2006, 2007; Skrbic and Burisic-Mladenovic, 2005).

High content of Cd is presumed to be ultimately related to phosphate fertilizers that are used in cultivation of sugar beet and cane (Skrbic and Burisic-Mladenovic, 2005). Likely, both plants are enriched in Cd due to formation of easily taken complex of Cd with phosphate (Skrbic and Burisic-Mladenovic, 2005). Although the majority of phosphate from processed plants is removed during juice purification by precipitating $Ca_3(PO_4)_2$, still a part of Cd can be present and distributed in subsequent stages or final sugar products (Skrbic and Burisic-Mladenovic, 2005).

The content of As in sugar is very low and most commonly depends on amounts of this element in cultivated soils and chemicals used for production of sugar beet (Sancho et al., 1998; Skrbic et al., 2003). An additional source of As in beet sugar is related to manufacturing processes (Sancho et al., 1998; Skrbic et al., 2003). Contents of Co and Ni are also very low and could be regarded as an evidence of no release of these elements from stainless steel during sugar manufacturing process (Sancho et al., 2000).

Certain correlations between concentrations of some elements in juice and sugar beet and their respective concentrations in sugar are established and described for samples coming from different factories (Skrbic and Burisic-Mladenovic, 2005; Mohamed, 1999; Awadallah et al., 1995). Accordingly, strong positive correlations for Cu, Co, Fe, and Zn between concentrations of these elements in sugar beet and sugar support the importance of planting, cultivating, and growing conditions as well as characteristics of soil on quality of the final stage product. Similarly, positive correlations for mentioned elements have been ascertained for products resulting from different stages of sugar production, i.e., molasses obtained from sugar beet (Skrbic and Burisic-Mladenovic, 2005). On the other hand, strong negative correlations between trace elements in sugar beet, different stage sugar products, and sugar are recognized to be a consequence of subsequent production stages (Skrbic and Burisic-Mladenovic, 2005). This can be observed, for example, in case of Fe and concentrations of this element in sugar beet and sugar and points out that the effect of technological lines, materials of equipment used for sugar processing, and additives included in sugar production can be significant (Skrbic and Burisic-Mladenovic, 2005).

In general, higher concentrations of elements such as Fe, Co, Cu, Mn, and Zn commonly result in increasing conductivity of sugar ash and affecting color of sugar solutions or crystals (Skrbic and Gyura, 2006; Mohamed et al., 1989). When both mentioned parameters are above certain specifications, sugar falls into a lower market category. Both natural (mineral soil composition and texture, botanical structure of sugar-rich plants) and processing-related (corrosion, evaporation, additives) sources of elements in sugar contribute to sugar contamination and cause differences in concentrations of some elements among samples of different country origins or even of the same locality that are quite remarkable (Mohamed et al., 1989).

INSTRUMENTAL METHODS OF SUGAR ANALYSIS

According to the International Commission for Uniform Methods of Sugar Analysis (ICUMSA), spectrophotometric (colorimetric) methods of sugar analysis are recommended for determination of traces of As, Cu, Fe, and Pb (ICUMSA accepted methods GS 2/3/9-25, GS 2/3-29, GS 2/3/7/8-31, and GS 2/1/3-27, respectively) in white refined sugar and other sugar processing products (ICUMSA, 2009). For determining K and Na in sugar beet, ICUMSA recommends using flame photometry (official method GS 6-7) (ICUMSA, 2009). In the case of As (tentative method GS 2/3-23) and Pb (official method GS 2/3-24) as well as As, Cd, Cu, and Fe (draft method 7), this institution suggests using atomic absorption spectrometry (AAS) with a heated graphite atomizer (GF-AAS, case of Cd, Cu, Fe, and Pb) in addition to a hydride generation atomizer (HG-AAS, case of As) for measurements of these elements in sugar. These methods are recognized to maintain necessary sensitivity and accuracy in sugar analysis without need for any additional preconcentration step (Skrbic and Gyura, 2006, 2007; Skrbic and Burisic-Mladenovic, 2005; Ronda et al., 2001; Sancho et al., 1998; ICUMSA, 2009; Miller-Ihli and Green, 1993; Miller-Ihli, 1994). Furthermore, ICUMSA is interested in improving the analytical methodology of analysis of white refined sugar and sugar-related products for the content of inorganic contaminants, mostly based on application of AAS as easily available, robust, and providing good analytical performance for trace analysis of sugar (Ronda et al., 2001; ICUMSA, 2009; Leblebici and Volkan, 1998).

Atomic Absorption Spectrometries

It is apparent from the literature that flame atomic absorption spectrometry (F-AAS) with an air-acetylene flame (Skrbic and Gyura, 2006, 2007; Skrbic et al., 2003, 2010; Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Mohamed, 1999; Waheed et al., 2009; Wojtczak, 2006; Leblebici and Volkan, 1998; Lew, 1972; Carbonell-Barrachina et al., 2002), GF-AAS (Miller-Ihli, 1994, 1995; Skrbic et al., 2003, 2010; Ronda et al., 2001; Sancho et al., 1997, 1998, 2000; Awadallah et al., 1984, 1985, 1986, 1995; Dias and Cardoso, 2006; Miller-Ihli and Greene, 1993; Miller-Ihli, 1994; Morris et al., 1976), and

HG/CV-AAS in the case of As and Hg (Sancho et al., 2001; Carbonell-Barrachina et al., 2002) are well-established element-specific detection techniques that are commonly used for analysis of white refined sugar and related products. Most commonly, F-AAS and GF-AAS are used to measure a limited group of elements, i.e., As, Cd, Cu, Fe, Hg, Mn, Pb, and Zn (see Table 3). Both atomic absorption spectrometric methods offer good analytical performance for these elements in reference to accuracy, precision, and fair resistibility to chemical interferences and other matrix effects. Additionally, their operation is simple and costs of instrumentation and maintenance are relatively low. F-AAS can also be used for determination of many more elements, including Ag, Au, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, and Zn, but in this case, analysis is time consuming (Mohamed, 1999).

Although atomic spectrometry offers the possibility of direct analysis of sugar, the sucrose matrix is recognized to cause interferences in F and GF atomization cells so strong that they typically hinder direct introduction of water solutions of sugar samples (Ronda et al., 2001; Sancho et al., 1998; Antonina and Allen, 2001). Matrix effects are related to high viscosity and surface tension of such sugar solutions and problems with a buildup on burners or graphite tubes of carbonaceous materials. When measuring moderately concentrated solutions of untreated sugar (dissolved only in water or a diluted HNO_3 solution), sucrose can easily melt and splash inside graphite tubes. Because Cd, Pb, and Zn are volatile, ashing temperature has to be kept below 500°C (Morris et al., 1976). Under such conditions, the organic matrix is not completely destroyed and charred in the atmosphere of inert gas that is a common type of GF-AAS analysis. As a result, carbon-containing residues cover graphite tubes, and serious interferences occur during atomization and absorption processes and impair results of analysis (Sancho et al., 1997; Dias and Cardoso, 2006; Morris et al., 1976). Usually, adequate dilutions of sugar samples may reduce these interferences, however, such a procedure can also decrease concentrations of elements in samples to levels below method detection limits (Sancho et al., 1997, 1998). To alleviate matrix effects, sugar samples are most commonly introduced into atomic spectrometers as solutions resulting from different decomposition procedures facilitated by use of oxidizing reagents (Ronda et al., 2001; Antonina et al., 2001). However, such procedures are inconvenient since they need time for handling and usually increase the risk of sample contamination and loss of elements to be measured (Ronda et al., 2001).

A digestion step can be avoided, thus reducing manipulation time and reagents used. In the case of GF, this can be achieved by applying adequate chemical matrix modifiers, i.e., $RhCl_3$, which added to a sample portion enables obtaining higher pyrolysis and atomization temperatures in a graphite tube (Dias and Cardoso, 2006). Good results are achieved using other matrix modifiers, i.e., $Mg(NO_3)_2$ (Miller-Ihli, 1994, 1995; Miller-Ihli and Greene, 1993) or Pd in conjunction with ascorbic acid (the latter reagent is added to a sample solution) (Ronda et al., 2001) and air-assisted ashing, which enhance oxidation of the organic matrix prior to atomization.

In general, F-AAS and GF-AAS are usually operated under instrumental conditions recommended by spectrometer manufacturers (Skrbic and Gyura, 2007; Skrbic et al., 2003, 2010; Skrbic and Burisic-Mladenovic, 2005; Leblebici and Volkan, 1998). Heating treatment required in GF-AAS measurements is also used as recommended or optimized to find drying, pyrolysis, atomization, and cleaning temperatures enabling the highest and the most reproducible response due to no loss of elements and low background signals (Miller-Ihli, 1994, 1995; Ronda et al., 2001; Dias and Cardoso, 2006; Miller-Ihli and Greene, 1993; Morris et al., 1976). Signals taken are background corrected using deuterium lamps or Zeeman correctors (Miller-Ihli, 1994, 1995; Skrbic and Gyura, 2006, 2007; Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Wojtczak, 2006; Ronda et al., 2001; Sancho et al., 1997, 1998, 2000; Dias aand Cardoso, 2006; Miller-Ihli and Greene, 1993; Leblebici and Volkan, 1998; Morris et al., 1976). Calibration graphs with standards containing the same amounts of acids used for sample decomposition or preparation are commonly applied (Skrbic and Gyura, 2006, 2007; Skrbic and Burisic-Mladenovic, 2005; Skrbic et al., 2003; Dias and Cardoso, 2006). Simple water standards are used for calibration as well (Miller-Ihli, 1994, 1995; Wojtczak and Krol, 2002; Wojtczak, 2006; Sancho et al., 1997, 1998, 2000, 2001; Awadallah et al., 1984, 1985, 1986, 1995; Miller-Ihli and Greene, 1993; Leblebici and Volkan, 1998; Morris et al., 1976). Calibration by standard additions is used for quantification of element concentrations to balance influence of matrix in samples and standards (Ronda et al., 2001; Morris et al., 1976).

Inductively Coupled Plasma Optical Emission Spectrometry

Inductively coupled plasma-optical emission spectrometry (ICP-OES) is applied for multielement analysis of white refined sugar where a variety of elements, including Ag, Al, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, K, La, Li, Mg, Mn, Na, Nb, Ni, P, Sb, Sc, Sn, Sr, Ti, V, and Zn, can be simultaneously determined in a relatively short time, offering a much higher sample throughput than atomic spectrometry methods (Awadallah et al., 1984, 1985, 1986, 1995). Because of extended linear dynamic ranges, ICP-OES is suitable for determinations of major elements of sugar (Ca, K, Mg, Na) and trace and ultratrace constituents that are difficult to measure by other methods, i.e., Cu, Li, P, Sn, and Zn (Awadallah et al., 1995) and As, Cd, Cu, Pb and Sn (Allen et al., 1997). Unfortunately, the magnitude of chemical and spectral interferences is relatively greater than in the case of F-AAS or GF-AAS and can vary from one element to another and due to matrix concentrations. A wavelength correction or application of internal standards for quantification is impractical in this situation, and, hence, destructive sample preparation treatment of sugar samples is rather required and preferred (Allen et al., 1997).

TABLE 3
Achievable detection limits (in ng g^{-1}) for different instrumental methods of white refined sugar analysis

Element	F-AAS	GF-AAS	CV/HG-AAS	ICP-OES	DP-CSV	INAA	DP-ASV
As		—^{a} (Awadallah et al., 1984, 1985, 1986, 1995), 22 (Ronda et al., 2001), 20 (Skrbic et al., 2003), 10 (Skrbic and Burisic-Mladenovic, 2005)	—^{a} (Leblebici and Volkan, 1998), 8 (Carbonell-Barrachina et al., 2002)	200 (Allen et al., 1997)	2 (Sancho et al., 1998)	70 (Waheed et al., 2009)	
Al						—^{a} (Mohamed et al., 1989; Awadallah et al., 1985, 1986, 1995)	
Cd	40 (Waheed et al., 2009)	0.3 (Skrbic et al., 2003), 0.15 (Skrbic and Burisic-Mladenovic, 2005), 0.13 (Ronda et al., 2001)		8 (Allen et al., 1997)			2 (Sancho et al., 1997)
Co	—^{a} (Mohamed, 1999)	2.7 (Ronda et al., 2001)			1.1 (Sancho et al., 2000)	—^{a} (Mohamed et al., 1989; Awadallah et al., 1985, 1986)	
Cr		1.5 (Ronda et al., 2001)				—^{a} (Mohamed et al., 1989; Awadallah et al., 1985, 1986)	
Cu	—^{a} (Mohamed, 1999l Leblebici and Volkan, 1998), 250 (Carbonell-Barrachina et al., 2002), 5 (Skrbic and Gyura, 2006, 2007), 0.5 (Wojtczak and Krol, 2002; Wojtczak, 2006)	3.4 (Ronda et al., 2001), 2 (Skrbic et al., 2003), 1.0 (Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005)		—^{a} (Awadallah et al., 1995), 7 (Allen et al., 1997)			2.5 (Sancho et al., 1998)
Fe	—^{a} (Mohamed, 1999; Leblebici and Volkan, 1998), 30 (Skrbic et al., 2003), 15 (Skrbic and Gyura, 2006, 2007), 1.5 (Wojtczak and Krol, 2002; Wojtczak, 2006)	1.0 (Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005)				—^{a} (Mohamed et al., 1989; Awadallah et al., 1985, 1986)	

(Continued on next page

TABLE 3
Achievable detection limits (in ng g^{-1}) for different instrumental methods of white refined sugar analysis *(Continued)*

Element	F-AAS	GF-AAS	CV/HG-AAS	ICP-OES	DP-CSV	INAA	DP-ASV
Hg			1 (Skrbic et al., 2003), 0.05 (Skrbic and Burisic-Mladenovic, 2005)			4 (Waheed et al., 2009)	0.5 (Sancho et al., 2001)
Mn	—[a] (Mohamed, 1999)	1 (Skrbic et al., 2003), 0.05 (Skrbic and Burisic-Mladenovic, 2005)				—[a] (Mohamed et al., 1989; Awadallah et al., 1985, 1986)	
Ni	—[a] (Mohamed, 1999)				3.4 (Sancho et al., 2000)		
Pb	—[a] (Mohamed, 1999; Leblebici and Volkan, 1998), 70 (Waheed et al., 2009)	—[a] (Awadallah et al., 1984, 1985, 1986, 1995), 9.5 (Dias and Cardoso, 2006), 5.9 (Ronda et aql., 2001), 5 (Skrbic et al., 2003), 3.3 (Miller-Ihli, 1994, 1995), 2.5 (Skrbic and Burisic-Mladenovic, 2005), 0.9 (Miller-Ihli and Greene, 1993)					2 (Sancho et al., 1997)
Sn		4.1 (Ronda et al., 2001)		—[a] (Awadallah et al., 1995), 75 (Allen et al., 1997)			
Zn	—[a] (Mohamed, 1999), 10 (Skrbic et al., 2003), 5 (Skrbic and Gyura, 2006, 2007), 0.5 (Wojtczak and Krol, 2002; Wojtczak, 2006)	2.5 (Ronda et al., 2001), 0.05 (Skrbic and Burisic-Mladenovic, 2005, 3)		—[a] (Awadallah et al., 1995)			1 (Sancho et al., 1997)
V						—[a] (Mohamed et al., 1989; Awadallah et al., 1985, 1986, 1995)	

[a] Not reported.

Stripping Voltammetry

Among electrochemical methods, differential-pulse anodic stripping voltammetry (DP-ASV) (11, 12, 20) and differential-pulse cathodic striping voltammetry (DP-CSV) (Sancho et al., 1998, 2000) are alternatively used to measure nutritionally and technologically relevant trace elements (As, Hg, Cd, Co, Cu, Ni, Pb, Zn) in sugar samples. As compared to atomic spectrometry, stripping voltammetry offers low maintenance costs in addition to attractively high analytical performance, i.e., sensitivity, detection power, selectivity, and simultaneity of measurements of a certain group of elements (Cd, Cu, Pb, Zn). It can be used to determine mentioned elements in digested samples or in untreated solutions of sugar. In the latter case, sample contamination from reagents or losses due to vigorous and long sample decomposition can be readily avoided. However, standard additions have to be applied for calibration to overcome possible matrix effects caused by sucrose and related to increasing solution viscosity and difficulties in diffusion of element ions toward electrode surfaces (Sancho et al., 1997, 1998). As compared to atomic spectrometry, voltammetric analyses of untreated sugar samples decrease a lot of analysis time and risk of contamination (Sancho et al., 1997), but the number of elements that can be determined with this method is limited. Additionally, base electrolyte buffers and other chemicals added in order to convert element ions into forms adequate for electrolysis can enhance risk of contamination.

Neutron Activation Analysis

Instrumental neutron activation analysis (INAA) has also found application in analysis of white refined sugar (Waheed et al., 2009; Awadallah et al., 1984, 1985, 1986, 1995). This method is nondestructive and presents high sensitivity with comparatively low detection limits for many major and trace elements. Additionally, minimal sample handling is normally required before measurements (grinding and powdering only) (Waheed et al., 2009; Awadallah et al., 1984, 1985, 1986), but samples can also be ashed (calcined) in order to pre-concentrate elements to be determined (Mohamed, 1999). Nevertheless, and despite all of this, INAA cannot be considered for routine analysis of sugar because of special and expansive instrumentation that is required to maintain measurements, in addition to experienced equipment operators. It is usually applied for multi-element analysis of sugar where many elements, including Al, Br, Cl, Ca, Co, Cr, Cs, Fe, K, Mg, Mn, Na, La, and Rb and Sc, As, Au, Ba, Ce, Cu, Dy, Eu, Hf, Lu, Sb, Se, Sm, Ta, Th, Tl, Ti, U, V, W, and Zn, are determined. Unfortunately, in the case of some elements such as Cd and Pb (Waheed et al., 2009) or Cu, Li, P, Sn, and Zn (Awadallah et al., 1995), detection limits achieved with INAA are poor, and other instrumental methods have to be used instead. INAA quite often serves as a reference method to ICP-OES measurements (Awadallah et al., 1984, 1985, 1986).

SAMPLE PREPARATION

Dry and Wet Ashings

According to ICUMSA, a wet ashing procedure aimed at decomposing sucrose with the aid of concentrated HNO_3 and 30% H_2O_2 solutions is recommended as sample treatment prior to determination of Pb by GF-AAS in sugar and related products (Miller-Ihli, 1994, 1995; ICUMSA, 2009). In brief, 1.5 g sugar samples (or 3.0 g portions of 50% (m/m) water sugar solutions) are just partially decomposed by heating at first with small amounts of HNO_3 and then with H_2O_2. Direct decomposition of resulting sample solutions occurs inside graphite tubes with atomization platforms, during a pyrolysis (ashing) step and in an atmosphere of O_2, which facilitates oxidation of organic compounds, and in the presence of $Mg(NO_3)_2$, which added as a matrix modifier stabilizes inorganic constituents in ash. Using the same GF configuration, 50% (m/m) water sugar solutions containing only HNO_3 at a concentration of 5.0% (m/v) could also be analyzed (Miller-Ihli and Greene, 1993). Although analytical performance of both described sample preparation procedures and GF-AAS methods of analysis is accepted as satisfactory (Miller-Ihli, 1995), the obligatory O_2-assisted pyrolysis step requires subsequently long cooling times to remove remnants of O_2 from the GF and to prolong the lifetime of graphite tubes. It seems as well that technical operation of such a system is difficult for routine analyses and demands some experience and expense. ICUMSA suggests using dry ashing with $Mg(NO_3)_2$ and MgO as ashing aids in the case of determination of As by GF-AAS and HG-AAS (ICUMSA, 2009). However, when mixed $Mg(NO_3)_2$ and MgO are applied, resulting ashes contain large amounts of solids, and, consequently, large volumes of acids usually have to be used for complete dissolution of residues (Leblebici and Volkan, 1998).

Amounts of sugar taken for analysis matter greatly when F-AAS is used for measurements. Larger samples are generally required because concentrations of trace elements are lower than detection limits offered by this method. Consequently, 100 g samples of sugar can be dry ashed with concentrated H_2SO_4 (Leblebici and Volkan, 1998) or its 10% solutions (Lew, 1972). Such gross sugar portions are charred at first using a simple burner. Afterwards, resulting samples are ashed by heating in a muffle furnace at 550°C for 2–3 days. Finally, noncombustible residues remaining are dissolved in a concentrated HCl solution (1:1) and diluted with water to 25 mL. Dry ashing of bulk sugar samples can also be completed using $Mg(NO_3)_2$ (ashing aid) in a combination with a concentrated HNO_3 solution (Leblebici and Volkan, 1998). In this case, ashing is carried out at 450°C for 1–2 days, then remnants are dissolved in a mixture of concentrated HCl and HNO_3 solutions (4:3) and diluted with water to 25 mL. Unfortunately, various sources of error should be considered in the case of sugar combustion and dry ashing. They include losses of some elements, especially Cd, Hg, Pb, Zn, As, and Sn, due to volatilization or to retention in ashing containers, sample contamination from ashing containers and furnaces, long ashing times (up to 3 days), and incomplete dissolution of resulting ashes.

Alternative procedures like wet ashing in open-vessel and closed-vessel microwave-assisted systems are often utilized instead of dry ashing. Lower sugar samples are used and they are typically oxidized in mixtures of concentrated reagents, i.e., HNO_3 with H_2SO_4 (Skrbic and Gyura, 2006, 2007), HNO_3 with $HClO_4$ (Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005; Waheed et al., 2009) and HNO_3 with H_2O_2 (Sancho et al., 1997; Allen et al., 1997), or HNO_3 alone (Mohamed, 1999; Awadallah et al., 1984, 1985, 1986, 1995; Carbonell-Barrachina et al., 2002). The resulting sample digest is subsequently diluted and analyzed by atomic spectrometric methods. Accordingly, well-mixed sugar as received portions (10 g) is dissolved in water (10 mL) at first, and then resulting aliquots are treated with a mixture of concentrated HNO_3 and H_2SO_4 solutions (1:1) by heating on a hot plate (Skrbic and Gyura, 2006, 2007). The dark residues that appear are treated next with a concentrated HNO_3 solution only until all sight of charring disappears. After cooling, water is added to remnants and all is evaporated by boiling. This procedure is repeated twice, and, finally, residues are dissolved in water and diluted to 50 mL. Sugar and other related samples from different stages of sugar production (4 g) can also be dried at 105°C for several hours and afterwards wet ashed only with a concentrated HNO_3 solution under a cover. When clear solutions are obtained, they are made up with water to 100 mL (Mohamed, 1999; Awadallah et al., 1984, 1985, 1986, 1995).

Even smaller amounts of sugar or related samples (1–2 g) can be digested by the wet oxidative decomposition similar to that described above (Skrbic and Burisic-Mladenovic, 2005; Waheed et al., 2009; Allen et al., 1997). Accordingly, samples or their water aliquots (1 g/4 mL) are charred at first with a concentrated HNO_3 solution and gently heated under a cover at 85–90°C on a hot plate. This prevents splashes and losses of As and Hg. Afterwards, concentrated $HClO_4$ (Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005; Waheed et al., 2009) or 30% H_2O_2 solutions (Allen et al., 1997) are added, and digestion is prolonged by heating samples until NO_x fumes stop evolving. Resulting clear solutions are dissolved to volume with water to 10 (Waheed et al., 2009; Allen et al., 1997) or 50 mL (Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005).

Microwave-assisted digestion procedures are also applied, however, they are not used as often as dry or wet ashings because much smaller samples of sugar (0.5 or 1 g) have to be taken for decomposition and analysis. To prevent a too vigorous course of reaction and overheating of vessels, sugar portions are dissolved at the beginning in water at proportions of 1/10 g/mL (Sancho et al., 1997, 1998, 2000, 2001) or 1/4 (g/mL) (Allen et al., 1997) to create homogeneous sample solutions. Resulting aliquots are digested in a mixture of concentrated HNO_3 and 40% (m/v) H_2O_2 solutions (1:2) (Sancho et al., 1997, 1998, 2000, 2001) or a concentrated HNO_3 solution (Allen et al., 1997). After digestion is completed, resulting solutions are diluted to 25 mL (Sancho et al., 1997, 1998, 2000, 2001; Allen et al., 1997).

It has been established that open-vessel digestion procedures can yield recovery and precision comparable to the case of closed-vessel microwave-assisted digestion procedures, despite the fact that the latter are recognized as reducing losses of elements and providing more uniform digestion (Allen et al., 1997). Additionally, lower detection limits can be obtained with open-vessel digestion procedures because of higher sample evaporation and solution volume reduction (Allen et al., 1997).

Direct Analysis

Although high-purity reagents are usually applied in dry and wet ashing sample decomposition procedures, airborne contamination can be observed and result in relatively high blank values, especially in the case of trace elements, i.e., Pb (Miller-Ihli, 1995) and Cu (Allen et al., 1997). Indeed, sample contamination can be a real problem in white refined sugar analysis, and, therefore, methods avoiding sample decomposition steps are demanded. Such methods without protracted sample preparation operations can certainly save time, minimize the likelihood of sample contamination, and fulfill green analytical chemistry principles (Ronda et al., 2001; Koel and Kaljurand, 2006). A very interesting procedure has been proposed by Wojtczak and Krol (Wojtczak and Krol, 2002; Wojtczak, 2006). In this sample treatment procedure, large sugar samples (100 g) are dissolved in water only, and then resulting solutions (400 mL) are filtered through 0.45 or 8.0 μm membrane filters to determine water-soluble and water-insoluble (retained on respective filters) forms of elements. Respective filtrates of sugar solutions are later treated with a strongly acid cation exchange resin, Bio-Rad 50W×4-100 (1.5 mL), filled in columns (see Fig. 2). By contacting sugar solutions with the resin, cationic element species are retained on column beds while sucrose is separated and goes to column effluents. To elute elements retained, resin beds are rinsed with a 5 mol L^{-1} HCl solution while respective eluates are collected and diluted prior to measurement of (Ca, Cu, Fe, Mg, Zn).

Direct analysis of sugar solutions by atomic spectrometry methods is rather uncommon. In such a case, sugar samples are dissolved in low concentrated HNO_3 solutions (0.03–0.16 mol L^{-1}) at a proportion of sample mass to solution volume of 1/25 (Dias and Cardoso, 2006) or 1/10 (Ronda et al., 2001). Ascorbic acid can be added to such solutions as a matrix modifier (Ronda et al., 2001). Sugar samples (5 g) can be ground to a fine powder, dried to constant mass at 105°C, and then dissolved in water and acidified with HNO_3 to pH = 2 in order to release elements bound by the organic sugar matrix (Skrbic et al., 2003). In both mentioned procedures, elements are subjected to analysis by GF-AAS without O_2-assisted ashing. An interesting green analytical chemistry procedure is yeast fermentation, in which sucrose is broken down to CO_2 and ethanol, both easily removed prior to the charring step in GF-AAS analysis (Morris et al., 1976). For that purpose, sugar samples (5 g or 10 g

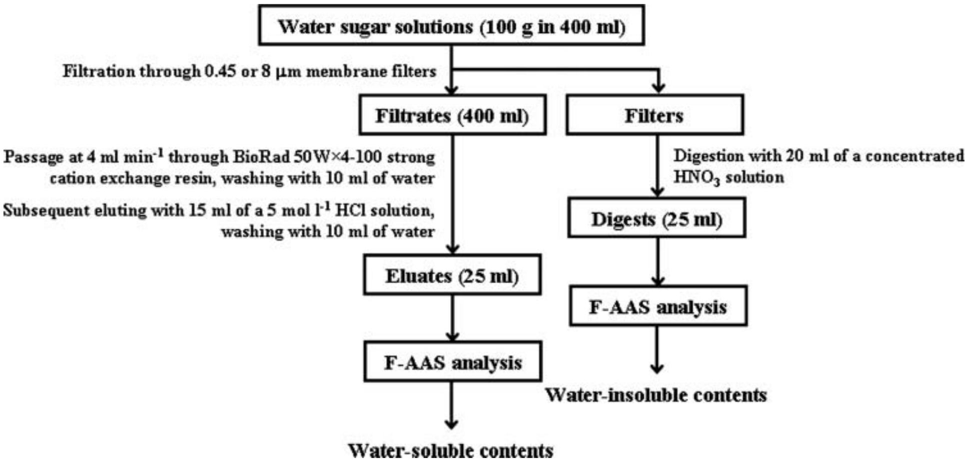

FIG. 2. Pre-concentration of trace elements using solid-phase extraction with a cation exchange resin prior to their determination by F-AAS (adopted from Wojtczak and Krol, 2002).

of sugar liquors) are treated with baker's yeast at 40°C, and after completing fermentation, yeasts are removed by centrifugation. Clear supernatants are diluted to 50 mL and subjected to analysis.

In the case of INAA analysis, sugar samples (2 g) are wet ashed, i.e., decomposed and evaporated to dryness, using a concentrated HNO_3 solution (Awadallah et al., 1995). In this way, respective residues obtained are ready for irradiation (Awadallah et al., 1995). Most commonly, however, they are only dried at 80–105°C, powdered by grinding, and directly submitted to irradiation and subsequent measurements (Waheed et al., 2009; Awadallah et al., 1984, 1985, 1986). Neither ASV or CSV measurements require sugar samples to be digested, certainly decreasing time of analysis and risk of sample contamination. Accordingly, sugar samples are dissolved and diluted with water at proportions of sample mass to solution volume of 1/10 (Sancho et al., 1997, 1998) or 1/12.5 (Sancho et al., 2000, 2001). Resulting solutions are adjusted to proper pH, i.e., below 1, with a HCl solution (Sancho et al., 1998), 5.6 or 5.0 using acetate buffers (Sancho et al., 1997, 1998), 9.2 with an ammonium buffer (Sancho et al., 2000), or mixed with a supporting electrolyte (Sancho et al., 2001), which is necessary for that kind of analysis. Solutions are also deoxygenated by purging with water saturated N_2 for 10 minutes (Sancho et al., 1997, 1998, 2000, 2001). For DP-CSV measurements of As, respective sugar solutions are spiked with Cu(II) ions and hydrazine sulfate (Sancho et al., 1998). DP-CSV determinations of Co and Ni require addition of a dimethylglyoxime solution to form metal complexes (Sancho et al., 2000).

It should be noted that other by-products resulting from subsequent stages of sugar production, i.e., molasses and brown sugar, are analyzed using the same instrumental methods of analysis and sample preparation techniques as in case of white and refined sugars (Skrbic and Burisic-Mladenovic, 2005; Mohamed, 1999; Mohamed et al., 1989; Awadallah et al., 1984, 1985, 1986, 1995; Dias and Cardoso, 2006).

QUALITY ASSURANCE AND CONTROL IN SUGAR ANALYSIS

A detailed verification of analytical performance of each method of sugar analysis is acknowledged as a critical part of the whole analytical procedure. It positively impacts quality of results obtained for unknown samples of sugar to be analyzed (Miller-Ihli, 1995). In terms of quality assurance (QA) and control (QC) of sugar analysis, selected criteria of quality are commonly evaluated, and this includes measurement precision (reproducibility) of the whole analytical procedure, detection and quantification limits (DL and QL), and accuracy.

In reference to precision, relative standard deviations (RSD) achieved for several parallel measurements of selected commercial sugars are frequently determined (Miller-Ihli, 1994, 1995; Skrbic and Gyura, 2006, 2007; Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Mohamed, 1999; Wojtczak, 2006; Ronda et al., 2001; Sancho et al., 1997, 1998, 2000, 2001; Dias and Cardoso, 2006; Miller-Ihli and Greene, 1993; Leblebici and Volkan, 1998; Morris et al., 1976; Allen et al., 1997). This precision for most of surveyed methods is usually within 2 to 8%. However, even higher RSD values, i.e., 10–20%, are regarded as confirming good repeatability and precision of replicate sample preparation procedures and measurements taken. DL values that represent the lowest concentrations of elements that can be dependably determined with proposed procedures are also determined as a part of QC and QA (see Table 3). They are typically in the ng g^{-1} range or lower and can differ within one technique due to a multiplicity of sample preparation procedures used or instrumental conditions applied for measurements.

Accuracy, which is related to correctness, is commonly evaluated by spike recovery experiments or analysis of certified reference materials (CRMs). In reference to recoveries, elements are added to selected sugar samples at different levels of fortification, i.e., from 10 to 200 ng g^{-1} or even up to 25 μg g^{-1}, and analyses of such samples are carried out (Miller-Ihli, 1994, 1995; Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Ronda et al., 2001; Sancho et al., 1997, 1998, 2000, 2001; Dias and Cardoso, 2006; Miller-Ihli and Greene, 1993; Leblebici and Volkan, 1998; Carbonell-Barrachina et al., 2002; Morris et al., 1976; Allen et al., 1997). Usually, recoveries produced in different measurement processes are within 83 to 126% or even better, and this proves reliability and reasonably good accuracy of sample preparation and measurement methods applied for sugar analysis (Skrbic et al., 2010; Skrbic and Burisic-Mladenovic, 2005; Wojtczak and Krol, 2002; Skrbic and Gyura, 2006; Ronda et al., 2001; Sancho et al., 1997, 1998, 2000; Dias and Cardoso, 2006).

Due to lack of a CRM of white sugar, CRMs of elements in other than sugar matrices, e.g., rye flour V-8 and hay powder V-10 from International Atomic Energy Agency (IAEA) (Skrbic and Gyura, 2006; Waheed et al., 2009), bushes, branches, and leaves GBW07603 from Institute of Geophysical and Geochemical Exploration of China (Carbonell-Barrachina et al., 2002), lake waters TM-25.2 and TMDA-54.3 from National Water Research Institute of Canada (Dias and Cardoso, 2006), water 1643c, typical diet 1548a, and citrus leaves 1572 from National Institute of Standards and Technology (Miller-Ihli, 1994, 1995; Waheed et al., 2009; Miller-Ihli and Greene, 1993; Carbonell-Barrachina et al., 2002), or other biological and environmental materials (Awadallah et al., 1995), are taken as control materials and analyzed to validate suitability of the whole procedure and test its accuracy and precision.

Results achieved for one analytical method can also be compared to those obtained by another independent method, i.e., DP-ASV or DP-CSV in unprepared samples and GF-AAS or HG-AAS (in the case of Hg) in digested samples (Sancho et al., 1997, 1998, 2000, 2001), GF-AAS in digested and just dissolved samples (Dias and Cardoso, 2006), F-AAS with INAA and ICP-OES analyses (Mohamed, 1999), and INAA with F-AAS analyses (Waheed et al., 2009).

CONCLUSIONS AND PERSPECTIVES

In terms of general food safety and control, as well as different processing applications of white refined sugar, its analysis for the content of trace elements is very important, with the results being very decisive for the sugar industry. It seems that great availability, ease in operation, and good analytical performance achieved with F-AAS and GF-AAS make them commonly applicable for routine analysis of sugar for the content of trace elements.

However, due to a complex matrix of sugar, which is pure sucrose with some inorganic and organic additives and contaminants, analyzed samples have to be transferred into solutions suitable for atomic absorption spectrometry measurements. Several digestion procedures has been proposed for that purpose, but in general, a sugar mineralization strategy is usually time-consuming and may increase the risk of sample contamination or element losses, which occur in wet or dry ashing procedures (Sancho et al., 1997, 1998).

Since analysis of sugar is an important part of food safety and quality control, it can be expected that more effort and development in the future will be focused on fast methods of direct sugar analysis using nondestructive sugar preparation procedures like ultrasound extraction (Chmilenko and Baklanova, 1998) and solid-phase extraction (Wojtczak and Krol, 2002; Wojtczak, 2006) or decomposition of sugar samples by yeast fermentation (Morris et al., 1976) or slurry sampling of partially carbonized samples (Baklanov et al., 2003). Such sample pre-treatments will certainly bring a number of advantages, counting reduced sample preparation and analysis times, decreased potential for defeat of elements, reduced risk of contamination coming from reagents, and enhanced sensitivity and detection power due to lower blanks and sample dilutions. Additionally, this category of sample preparation is considered to be "green."

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