

Analytical, Nutritional and Clinical Methods Section

Determination of nickel and cobalt in refined beet sugar by adsorptive cathodic stripping voltammetry without sample pretreatment

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Abstract

Nickel and cobalt have been analysed in refined beet sugar at the $\mu\text{g kg}^{-1}$ level by adsorptive cathodic stripping voltammetry in the differential-pulse mode (DPCSV) at the hanging mercury drop electrode (HMDE) as their dimethylglyoxime complexes, $\text{M}(\text{DMG})_2$. Measurements were directly carried out on untreated sugar solutions. The performance of the procedure was compared with electrothermal atomic absorption spectrometry (ETAAS) applied to digested sugar samples, and showed in general better accuracy. The procedure was applied to the determination of these toxic elements in refined beet sugar samples, and concentrations below $50 \mu\text{g kg}^{-1}$ nickel and $10 \mu\text{g kg}^{-1}$ cobalt were found, which are much lower than the toxic levels of these elements. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Cobalt is essential to humans but must be supplied in the diet entirely in its physiologically active form, vitamin B_{12} , as the tissues are unable to synthesise the vitamin from dietary cobalt (Thunus & Lejeune, 1994; Underwood, 1977). Nickel is a component of the enzyme urease and as such is considered essential to plants (Anke, Angelow, Glei, Mueller & Illing, 1995; Schaller, Raitzel & Angerer, 1994; Underwood, 1977). Essentiality of this element to man remains controversial and unproven. However, the facts that nickel is present in all human tissue and that there is evidence for its homeostatic control, strongly suggest that nickel is required by humans (Gammelgaard & Jøns, 1995).

Reported data for the cobalt and nickel contents of human foods and total diets are both meagre and highly variable. Some of the variation undoubtedly stems from analytical errors or inadequacies, but some also reflects soil and climatic differences directly affecting the metal content of foods of plant origin and indirectly those of animal origin. Nutritional habits and food processing

technologies also affect the intake of these elements through food.

In a study of diets of children in USA, Murthy, Rhea and Peeler (1971) found total Co intake to vary from 0.30 to 1.77 mg day^{-1} . These levels are much higher than the mean of $29 \mu\text{g day}^{-1}$ for French adult diets recently reported by Biego, Joyeux, Hartemann and Debry (1998), $11 \mu\text{g day}^{-1}$ estimated by Dabeka and McKenzie (1995) in Canada, or the levels below $1 \mu\text{g Co day}^{-1}$ estimated for Japanese diets (Shimbo et al., 1996). Among individual types of foods, the green leafy vegetables are the richest in Co content ($0.2\text{--}0.6 \text{ mg kg}^{-1}$ dry sample), while dairy products, refined cereals, and sugar are the poorest ($0.01\text{--}0.03 \text{ mg kg}^{-1}$ dry sample).

Cobalt has a low order of toxicity in all species studied, including man. Daily doses of 3 mg Co kg^{-1} body weight may be tolerated by sheep for many weeks without visible toxic effects (Underwood, 1977). Nevertheless, ingestion or inhalation of large doses leads to pathological disorders.

Nickel is relatively non-toxic, so that Ni contamination of foods does not present a serious health hazard. Food processing has been demonstrated to take up negligible amounts of nickel from steel containers (Flint & Packirisamy, 1997). In acidic conditions, a higher amount of

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nickel may be released, but it is poorly absorbed and causes no detectable damage.

The nickel content in food has attracted very little attention so far as it is present at a very low concentration in refined foods and most foods of animal origin. Total dietary nickel intakes vary greatly with the amounts and proportions of foods of animal (low content) and plant (high content) origin consumed and with the amounts of refined and processed foods such as white sugar and flour included in the diets. Recent surveys in Western countries have estimated the nickel dietary intake of an adult human to range from 100 to 300 $\mu\text{g day}^{-1}$ (Dabeka & McKenzie, 1995; Seifert & Anke, 1999; Uthus & Seaborn, 1996). However, dietary intakes of nickel and cobalt are decreasing due to changes in the nutritional habits of western citizens (Seifert & Anke).

Control of trace metals in sugar is very important because of its fundamental nutritional role in the diet of humans. There is a lack of available data of nickel and cobalt contents in sugar, but it is supposed that they may vary considerably as they depend not only on the sugar processing practices, but also on the type of soil in which the sugar beet was grown. At the moment, maximum admissible levels of nickel and cobalt in refined sugar have not been regulated, although they can well be considered similar to those established for metals of similar toxicity such as copper (2 mg kg^{-1}). However, it is predictable that these levels will be soon regulated as an increasingly important aspect of sugar quality is to control the concentration of trace metals and to minimise sugar pollution by improving husbandry and processing practices.

The International Commission for Uniform Methods of Sugar Analysis (ICUMSA) recommends spectrophotometric methods for the determination of most heavy metals in sugar (ICUMSA, 1994), but the technique lacks of the necessary sensitivity to determine accurately the low metal levels usually found in refined sugar (in the $\mu\text{g kg}^{-1}$ range). More sensitive electrothermal atomic absorption spectrometric (ETAAS) methods are usually applied to the determination of Ni and Co in food products (Barbera & Farre, 1988; Capar, 1990; Gottelt, Henrion, Kalahne & Stoyke, 1996; Viñas, Campillo, López & Hernández, 1995). However, the analytical matrix of sugar is expected to cause strong interferences in the graphite furnace, thus hindering the direct measurement of the metal in the sample, which must be digested prior to the determination, or the metal extracted and preconcentrated. This inconvenience causes this procedure to be time-consuming and increases the risk of sample contamination and loss of analyte.

Stripping voltammetry has attracted considerable attention for the determination of trace metals, as it combines low maintenance costs with good accuracy and precision and excellent sensitivity. The low detection

limits achieved are the result of performing the pre-concentration steps directly into the voltammetric cell, thus decreasing the sampling handling and thus the risk of sample contamination. Adsorptive cathodic stripping voltammetry (CSV) is a well established technique for trace determination of nickel and cobalt as their dimethylglyoxime complexes in a variety of matrixes such as alloys, food, biological materials or environmental samples (Adeloju, Bond & Briggs, 1984; Economou & Fielden, 1993; Ostapczuk, Valenta, & Nürnberg, 1986; Pihlar, Valenta & Nürnberg, 1981; Zhang, Wollast, Vire & Patriarche, 1989), and can be considered as a serious alternative to ETAAS for this purpose (Buldini, Ferri & Nobili, 1991).

In previous works, stripping voltammetric methods for the determination of zinc, cadmium and lead (Sancho, Vega, Debán, Pardo & González, 1997), and of copper and arsenic (Sancho et al., 1998) in undigested sugar samples have been described, and their performance compared to that of ETAAS and stripping voltammetry in digested samples. In this paper, an accurate and reproducible differential-pulse cathodic stripping voltammetry (DPCSV) method for the direct determination of low levels of Ni^{II} and Co^{II} in untreated solutions of refined beet sugar is described. Results are compared to those obtained by ETAAS for digested sugar samples. The proposed method has been applied to the determination of these trace metals in refined sugar produced by different Spanish beet sugar refineries.

2. Materials and methods

2.1. Apparatus and reagents

Stripping voltammetric experiments were carried out with a Metrohm (Herisau, Switzerland) E-506 polarograph connected to a Metrohm E-608 control unit and a Metrohm 663VA electrode used in the hanging mercury drop electrode (HMDE) mode. A platinum rod and an $\text{Ag}/\text{AgCl}, \text{KCl}_{\text{sat}}$ electrode were used as auxiliary and reference electrodes, respectively.

ETAAS measurements were performed with a Varian (Palo Alto, CA, USA) SpectrAA-800 spectrometer equipped with Zeeman GTA-100 background correction and a PSD-100 programmable sample dispenser.

Sugar samples were digested in a Milestone (Sorisole, Italy) MLS 1200 microwave oven. pH measurements were made with a glass-combined pH electrode connected to a Metrohm Model 654 pHmeter.

Solutions were prepared dissolving analytical-grade reagents in ultrapure water obtained by passing redistilled water through a Barnstead (Dubuque, IA, USA) Nanopure II water purification system. Standard solutions of nickel and cobalt were daily prepared by dilution of Carlo Erba (Milano, Italy) AAS standards (1000 mg

l^{-1}). Saccharose standard solutions were prepared by dilution of extrapure saccharose (Merck, Darmstadt, Germany) and stored at 4°C. Ammonia buffer solution (0.1 M) of pH 9.2 was prepared by mixing 1.9 ml of concentrated ammonia (13.4 M) and 1.2 ml of concentrated hydrochloric acid (11.6 M), and diluting to 250 ml. A 0.1 M dimethylglyoxime (DMG) solution was prepared by dissolving the appropriate amount of DMG in 95% ethanol, and was used without further purification. Concentrated nitric acid and 40% m/v hydrogen peroxide were used for sample digestion. Mercury used in the HMDE electrode was triply distilled.

Glassware and plasticware were soaked in 2 M nitric acid for 24 h and then rinsed thoroughly with deionized water.

2.2. Procedures

2.2.1. Sample digestion

Concentrated nitric acid (5 ml) and 10 ml of 40% m/v hydrogen peroxide were added to 0.5 g of extrapure saccharose dissolved in 5 ml of deionized water. This solution was placed in a 100 ml PTFE vessel and introduced 20 min in the microwave oven for digestion. The power of the magnetron was linearly increased from 250 to 600 W during the process. After digestion of organic matter, the resulting solution was diluted to 25 ml with deionized water. A control reagent blank was conducted simultaneously.

2.2.2. ETAAS measurements

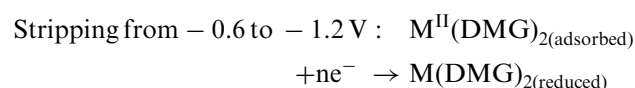
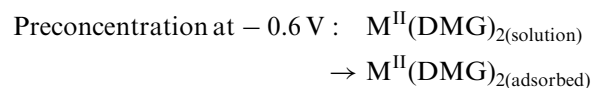
Sugar melts easily covering the graphite furnace with caramel, thus causing strong interferences and hindering the accurate measurement of the metal; a further dilution of the sample would reduce this interference, but decreases the metal content below the detection limit of the technique. Therefore, ETAAS was only applied to digested saccharose samples. Metal contents were obtained from the respective calibration plot (absorbance vs. concentration) by interpolation. Temperatures of atomization and wavelengths used for Ni and Co were, respectively: 2600°C and 232.0 nm (Ni), and 2300°C and 240.7 nm (Co).

2.2.3. DPCSV measurements

The optimal conditions for nickel and cobalt determination in sugar were partially adapted from existing literature (Adelaju et al., 1984; Ostapczuk et al., 1986; Pihlar et al., 1981; Zhang et al., 1989). Nickel and cobalt were determined in non-digested samples of pure saccharose and refined sugar. 2.0 g of untreated saccharose (or refined sugar where indicated) were dissolved in 25 ml deionized water and placed in the voltammetric cell. The solution was then spiked with 500 μ l of 0.1 M ammonia buffer (pH 9.2) and 100 μ l of 0.1 M DMG to form the

metal complexes, $M(\text{DMG})_2$. The solution was deoxygenated for 10 min by purging with water-saturated nitrogen. A clean mercury drop was extruded and the deposition potential was set to -0.6 V for 60 s, whilst the solution was stirred at 1920 rpm, in order to pre-concentrate the complexed metals onto the HMDE by adsorption. Then the stirrer was stopped and the electrode potential kept at -0.6 V for another 30 s; thereafter the potential was scanned towards more negative values at a scan rate of 20 mV/s, and using a superimposed differential-pulse of 50 mV of amplitude. The nickel and cobalt stripping peaks were registered at around -0.9 and -1.0 V, respectively (the actual potentials depend on the saccharose concentration), and their currents used as a measure of metal concentration. The standard additions method was used to calibrate the DPCSV sensitivity and to check linearity of response.

There is a controversy about the electrodic mechanism involved in the stripping reduction of the adsorbed complexes of nickel and cobalt, since the reduction of the cation to the elemental state involving two electrons (Pihlar et al., 1986) and the reduction of the ligand itself (Vukomanovic, Page & van Loon, 1996) have been proposed. In a simplified manner, the electrode reaction mechanism can be written as:



3. Results and discussion

3.1. Effect of saccharose concentration

The influence of saccharose concentration on the DPCSV peaks of Ni and Co are depicted in Fig. 1. Increasing amounts of extrapure saccharose were added to a solution of 20 mM ammonia buffer (pH 9.2) and 4×10^{-4} M DMG containing Ni^{II} and Co^{II} at a concentration of 36 $\mu\text{g l}^{-1}$, and the DPCSV peaks were registered in the conditions described above. Peak currents of nickel and cobalt were found to decrease by 50% in the presence of about 60 and 170 g l^{-1} of saccharose, respectively, and were completely suppressed at saccharose concentrations higher than 600 g l^{-1} . This interference is likely due to the increase of solution viscosity with increasing sugar concentration, which results in a more difficult diffusion of the metal towards the electrode surface (the diffusion coefficient decreases) (Khoulif, Jambon, Chatelut & Vittori, 1993) and hence

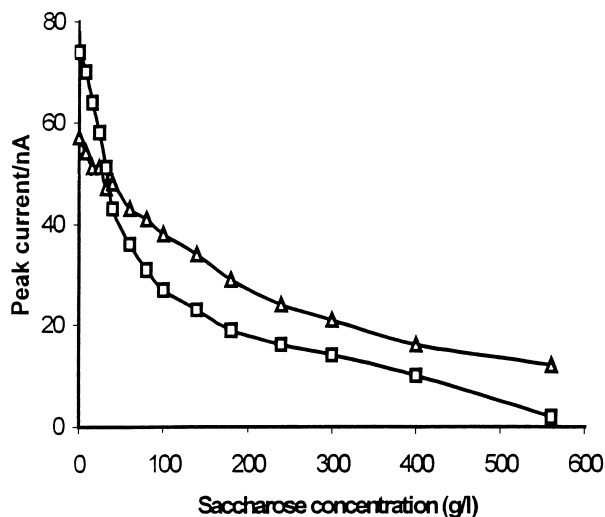


Fig. 1. Effect of the concentration of extra-pure saccharose on the DPCSV peaks of $36 \mu\text{g l}^{-1}$ nickel (\square) and cobalt (Δ).

in a decrease of the peak current. Peak potentials were also found to slightly shift towards more negative potentials with increasing sugar concentration, but the variation over the whole range of concentrations tested ($0\text{--}600 \text{ g l}^{-1}$) was only of 10 mV.

The matrix effect caused by saccharose can be overcome by using the standard additions method. The DPCSV sensitivity to Ni and Co in non-digested solutions of 80 g l^{-1} sugar was calculated from the slope of the regression line obtained by the standard additions method using a deposition period of 60 s, and resulted in 35 and $29 \text{ nA } \mu\text{g}^{-1}$ for nickel and cobalt, respectively. When the saccharose concentration was reduced to 40 g l^{-1} , the sensitivity increased to $45 \text{ nA } \mu\text{g}^{-1}$ (Ni) and $46 \text{ nA } \mu\text{g}^{-1}$ (Co) for the same deposition time.

3.2. Comparison of analytical methods

Aliquots of 25 ml of extrapure saccharose solutions were spiked with different concentrations of Ni^{II} and Co^{II} ranging from 62.5 to $625 \mu\text{g metal kg}^{-1}$ saccharose. Metals were then determined by ETAAS (Ni and Co) in digested samples, and by DPCSV (Ni and Co) in non-digested solutions, as described in the Procedures section. Reagent blanks for ETAAS and DPCSV were prepared from extrapure saccharose and measured in the same conditions. Experimental results are compiled in Table 1.

To assess the accuracy of the analytical procedures applied, linear regressions were obtained from the measured concentrations. Measured metal concentrations were plotted vs. added metal. Table 2 shows the calculated slope (p), intercept (q), and determination coefficient (R^2) of the regression line for each metal and procedure. If the method tested is not affected by systematic errors (bias), added and measured concentration must coincide,

i.e. the regression line will have a zero intercept and a slope and correlation coefficient of 1. As random errors can occur, slope and intercept of the regression line have confidence intervals that are expressed as:

$$p \pm ts_p$$

$$q \pm ts_q$$

where p and q are the slope and intercept, respectively; s_p and s_q are their standard deviations; t is the Student's t statistical parameter for $n-2$ degrees of freedom and 95% significance level (in this case t is 2.306), and n is the number of points of the regression line ($n = 10$).

Linearity of the calculated regression lines was assessed by means of an analysis of the residuals and by an F -test. The analysis of the residuals (not shown) was carried out and their normal distribution was verified applying the rankit normality plot test, which represents cumulative frequencies vs. the residuals arranged from the smaller to the higher values (Massart, Vandeginste, Buydens, De Jong, Lewi & Smeyers-Verbeke, 1997). The rankit normality plot showed to be linear for each of the four regression lines, and confirmed that residuals were normally distributed with zero mean, which demonstrates the goodness of fit of the linear regression models.

Further assessment of the linearity of the regression lines was achieved by means of the F -test of linearity. An analysis of variance of the regression lines was carried out, and the F -variance ratio calculated as *mean squares (variance) of the regression/mean squares of the residual* (see Table 2). F -values were in all cases much higher than the critical value [$F_{(1,8; 95\%)}$ is 5.318], thus confirming the linearity of the regression models for the concentration range tested. As linearity increases with increasing F , it can be concluded from Table 2 that DPCSV applied to non-digested sugar solutions yielded the highest linearity for cobalt, whereas highest linearity for nickel determinations was achieved using ETAAS.

As can be seen in Table 2, some of the intercepts and slopes of the regression lines obtained for the tested procedures differ significantly from 1 and 0, respectively, i.e. these theoretical values are not within the confidence interval, thus pointing to the existence of bias. Nickel determination in non-digested sugar samples by DPCSV can be accurately achieved since slopes and intercepts do not differ significantly from the expected values of 1 and 0, respectively. ETAAS measurements of Ni in digested samples showed to be affected by bias as both slope and intercept differ from their theoretical values, therefore hindering the accurate determination of this element in sugar. The slope and intercept obtained for Co by ETAAS over the concentration range tested do not differ from the expected values, thus indicating that this method is adequate for the accurate determination of Co in sugar samples. Finally, the

Table 1

Determination of Ni and Co in standard solutions of 80 g l⁻¹ extra-pure saccharose by ETAAS (digested samples) and DPCSV (non-digested samples)

Metal added ($\mu\text{g kg}^{-1}$)	ETAAS (digested)				DPCSV (non-digested)			
	Ni		Co		Ni		Co	
	Measured ($\mu\text{g kg}^{-1}$)	Recovery (%)	Measured ($\mu\text{g kg}^{-1}$)	Recovery (%)	Measured ($\mu\text{g kg}^{-1}$)	Recovery (%)	Measured ($\mu\text{g kg}^{-1}$)	Recovery (%)
62.5	86.1	137.7	71.9	115.0	74.5	119.2	82.5	132.0
125.0	149.9	119.9	136.8	109.4	116.0	92.8	124.7	99.8
187.5	222.3	118.6	180.8	96.4	201.5	107.5	214.5	114.4
250.0	302.0	120.8	245.6	98.3	248.2	99.3	251.4	100.6
312.5	375.0	120.0	314.0	100.5	306.8	98.2	320.1	102.4
375.0	431.3	115.0	411.4	109.7	370.4	98.8	401.6	107.1
437.5	497.5	113.7	401.6	91.8	430.1	98.3	459.6	105.0
500.0	560.8	112.2	582.0	116.4	536.4	107.3	546.8	109.4
562.5	610.5	108.5	594.6	105.7	565.7	100.6	612.1	108.8
625.0	691.3	110.6	649.5	103.9	632.3	101.2	670.4	107.3

determination of Co in non-digested sugar solutions by DPCSV has demonstrated to be affected by bias. The confidence interval of the intercept includes the expected value of zero, but the slope differs significantly from 1 (is slightly higher than 1) suggesting that, as the concentration of Co increases, the measured concentration is significantly higher. Therefore, at high cobalt concentrations the method does not give accurate results.

As Table 2 shows, the procedure more accurate for Ni determination in sugar is DPCSV. For Co determination, ETAAS should be chosen, but at the low Co concentration usually found in real sugar samples, DPCSV in non-digested sugar solutions is again preferred because it is faster and cheaper, and its accuracy is adequate for these samples. Therefore, the direct determination of Ni^{II} and Co^{II} by DPCSV in untreated sugar samples is proposed.

3.3. Performance characteristics of the procedure

The detection limits of the proposed procedure for the investigated metals were calculated as $\bar{x}_b + 3\sigma_b$, where \bar{x}_b and σ_b are the average concentration and the standard deviation, respectively, of five determinations of a blank of 100 g l⁻¹ extra-pure saccharose. These values were 3.4 $\mu\text{g kg}^{-1}$ sugar for nickel and 1.1 $\mu\text{g kg}^{-1}$ for cobalt.

The precision (expressed as repeatability) of the selected procedure was investigated by measuring the concentration of nickel and cobalt in different refined sugar samples. Five replications were carried out and average values (\bar{x}), their confidence intervals ($ts/n^{1/2}$) and the relative standard deviations ($100s/\bar{x}$) were calculated (see Table 3). The low standard deviations obtained (< 11%) indicate the good repeatability of the procedure. It can thus be concluded that nickel and

Table 2

Investigation of the occurrence of systematic errors by linear regression of the analytical procedures tested^a

Regression parameter	Metal	ETAAS (digested)	DPCSV (undigested)
Slope ($p \pm ts_p$)	Ni	1.067 \pm 0.040	1.014 \pm 0.059
	Co	1.064 \pm 0.126	1.073 \pm 0.052
Intercept ($q \pm ts_q$)	Ni	25.793 \pm 15.494	-0.207 \pm 22.727
	Co	-6.993 \pm 48.758	-0.647 \pm 20.033
Determination coefficient (R^2)	Ni	0.9979	0.9950
	Co	0.9794	0.9965
Variance ratio (F) ^a (linearity test)	Ni	3794	1590
	Co	381	2296

^a $F_{(1,8,\alpha=0.05)}$ is 5.318.

cobalt can be directly determined in untreated sugar solutions by DPCSV.

3.4. Determination of trace metals in refined beet sugar samples

The proposed procedure was applied to the determination of nickel and cobalt in 10 refined sugar samples supplied by different Spanish sugar beet refineries. Mean metal concentrations obtained from five determinations are shown in Table 4. From these results it can be concluded that nickel presents higher variations in sugar samples, its concentration ranging from levels below the detection limit (3.4 $\mu\text{g kg}^{-1}$) to 32 $\mu\text{g kg}^{-1}$ sugar. Cobalt content was below the detection limit (1.1 $\mu\text{g kg}^{-1}$) in most samples.

Finally, it can be deduced from these results that nickel and cobalt contents in refined white sugar produced

Table 3

Precision of DPCSV determination of trace metal contents in untreated sugar samples ($n=5$) expressed as confidence interval of the mean, and relative standard deviation (RSD)^a

Sample	Metal concentration ($\mu\text{g kg}^{-1}$ sugar)		RSD (%)	
	Ni	Co	Ni	Co
a	22.1±1.89	5.2±0.67	6.9	10.4
b	20.5±0.81	5.5±0.23	3.2	3.3
c	15.4±0.29	1.3±0.09	1.5	5.8
d	15.6±0.27	n.d. ^b	1.4	
e	20.1±0.70	2.5±0.13	2.8	4.2

^a Value of the Student's variable t for 4 degrees of freedom and $P=0.05$ is 2.776.

^b n.d., not detected.

Table 4

Levels of Ni and Co in quality sugar produced by Spanish sugar beet refineries

Sugar sample	Metal concentration / $\mu\text{g kg}^{-1}$ sugar	
	Ni	Co
1	16	n.d. ^a
2	22	5
3	32	n.d.
4	n.d.	n.d.
5	28	n.d.
6	20	5
7	n.d.	n.d.
8	15	n.d.
9	17	n.d.
10	28	n.d.

^a n.d., not detected.

in Spanish sugar refineries are much lower than the concentrations of heavy metals allowed by the current regulations (in the range of 1–2 mg kg^{-1} , depending on the toxicity of the element) (Real Decreto 1261/1987, 1987). No evidence of nickel release from stainless steel during sugar manufacturing has been found.

4. Conclusions

DPCSV can be used as an alternative method to ETAAS to determine low concentrations of nickel and cobalt in refined beet sugar. DPCSV has the advantage that both metals can be determined simultaneously and no sample pre-treatment is necessary, thus the analysis time and the risk of sample contamination are considerably decreased.

The method has been demonstrated to perform conveniently for metal determination in beet sugar of good quality (low metal concentration) produced by Spanish sugar refineries.

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