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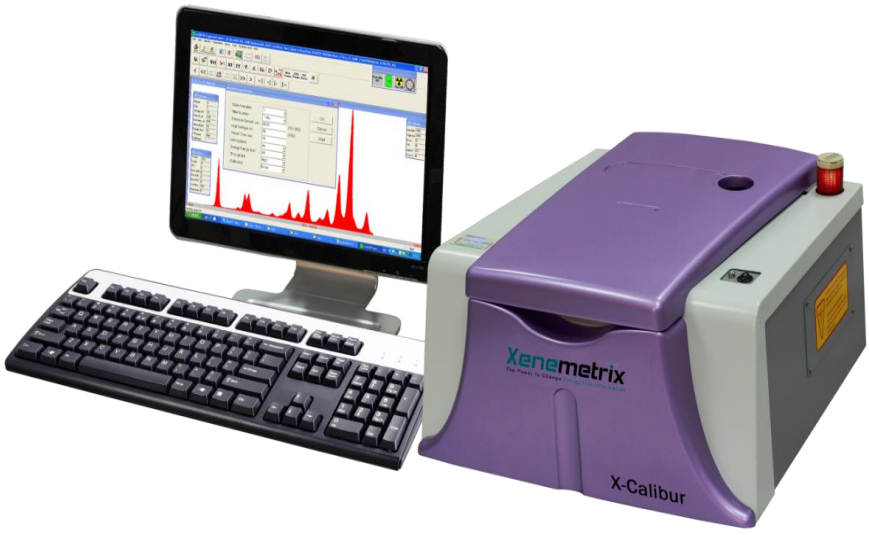
Quantitative analysis of Fe, Zn, Cu, Ni and Cr in Cocoa samples and S in Beet Molasses sample

EDXRF Analyzer: X-Calibur

Equipped with Silicon Drift Detector (SDD)



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Quantitative analysis of Fe, Zn, Cu, Ni and Cr in Cocoa samples and S in Beet Molasses

Abstract

A set of different format of Cocoa samples and one Beet Molasses sample were qualitatively and quantitatively analyzed by Xenemetrix X-Calibur bench top EDXRF analyzer equipped with highly efficient and sensitive silicon Drift Detector (SDD).
The analysis was performed with crude sample without any sample preparation. Calibration curves for each element were built with commercial certified standards in water.

Objective

- Quantitative and analysis of:
    1. Fe in cocoa powder sample.
    2. S in Beet molasses sample.
    3. Ni, Zn, Cr, Cu and Fe in Cocoa cake sample
    4. Ni, Zn, Cr, Cu and Fe in Cocoa mass sample.
- To demonstrate the instrument repeatability.
- To study the homogeneity of several samples

Background

EDXRF is an ideal analytical technique for qualitative and quantitative elemental analysis. EDXRF poses many advantages: 1) non destructive technique, 2) samples are analyzed with minimal preparation, 3) simultaneous analysis of many elements, 4) quick technique; typical analysis time is usually a few minutes, 5) ease of use for non-technical stuff, 6)automated analysis process, 7) flexibility of sample form; sample may be solid, powder, liquid or thin film form. These advantages have increased the popularity of XRF among industries such as chemicals, polymer and food.

Analytical Configuration

Table 1: Instrumental analytical configuration

Instrument	X-Calibur SDD Benchtop system
Anode	Rh-Anode X-ray Tube, 50 W
Detector	Silicon Drift Detector (SDD)
Environment	Helium for Sulfur Air for the other elements
Excitation mode	Direct excitation
Type of analysis	Regression analysis.
Sample Preparation	Three Cocoa samples and one Beet Molasses sample were analyzed as is in special XRF sample cups with thin film support.

Experimental and Results

Three different types of cocoa samples and one Beet Molasses sample were received for quantitative analysis. The analyzed elements and their expected concentrations for each sample are shown in table #2. (The elements of interest and their expected concentrations based on analysis performed with other techniques are shown in Table 2.)

Table 2: Samples list

Sample ID	product	Elements of interest	Expected concentrations [ppm]
1302948	Cocoa powder	Fe	589ppm
1302962	Beet Molasses	S	2000ppm
1303256	Cocoa Cake	Ni, Zn, Cr, Cu and Fe	12ppm, 80ppm, 4ppm, 45.9ppm and 371ppm accordingly (skip accordingly)
1303254	Cocoa Mass	Ni, Zn, Cr, Cu and Fe	606ppm, 45ppm, 2.1ppm, 45.9ppm and 207 ppm accordingly (skip accordingly)

No certified Cocoa calibration standards were provided for calibration of X-Calibur SDD analyzer. Therefore, the analyzer was calibrated with certified reference standards of the following elements Fe, Cu, Ni, Zn, Cr and S. For each calibration curve, two standards were used: Blank and 1000ppm. (Typical calibration curves are shown in figures #2 and #4)
The typical spectra of different types of Cacao samples were acquired using different acquisition parameters according to customer elements of interest to be analyzed in each sample.

Static precision tests were performed on all the samples to show the repeatability of X-Calibur Analyzer. The precision was performed by acquiring the spectra ten times without moving the sample between acquisitions. The repeatability results; i.e. the measured average concentration±1 standard deviation and relative standard deviations are shown in tables # 3, 4, 6 and 8.

Homogeneity tests were performed on Beet Molasses, Cocoa Cake and Cocoa Mass samples.
In order to study the homogeneity of Beet Molasses, Coco Cake and the Cocoa Mass samples, three different portions of each sample package were analyzed. The acquired spectra were analyzed quantitatively and the precision for each element in each sample was calculated.(see tables #5, 7 and 9).

Cacao powder sample

Figure 1: typical spectrum of a cocoa powder sample

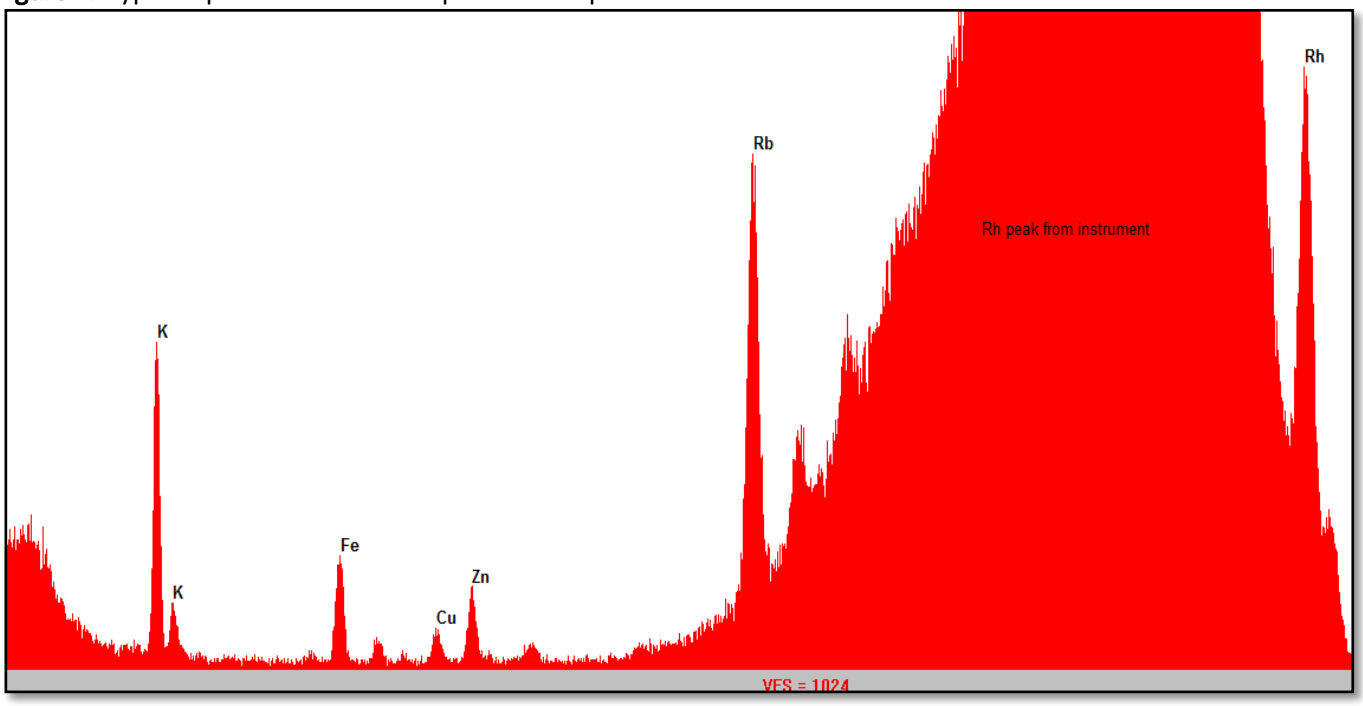

Figure 2: Fe calibration curve

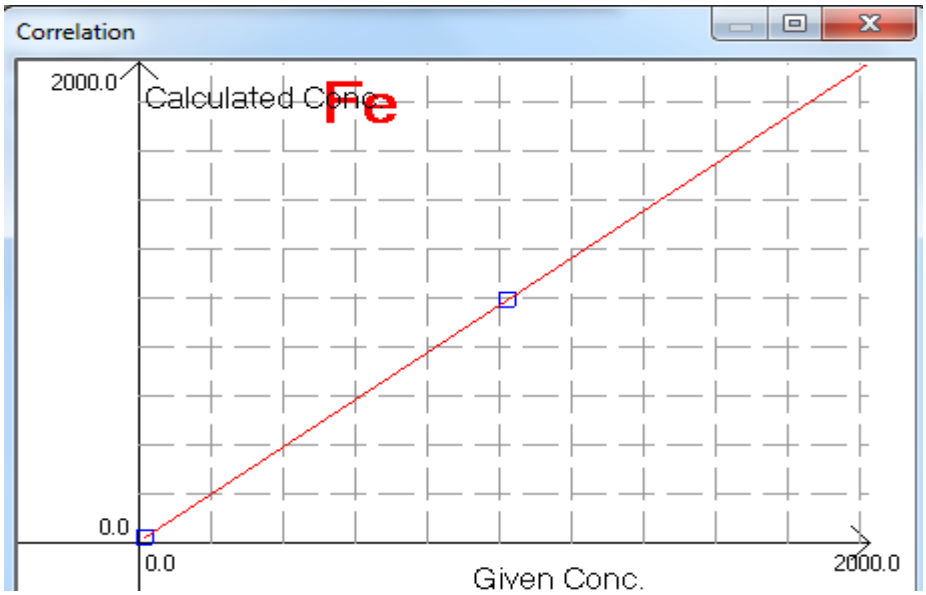

Table 3: Cacao powder statistic precision test result (N=10)

Element	Mean value [ppm]	standard deviation [ppm]	RSD [%]
Fe	601.0	39.5	6.6

Beet Molasses sample

Figure 3: typical spectrum of Beet Molasses sample

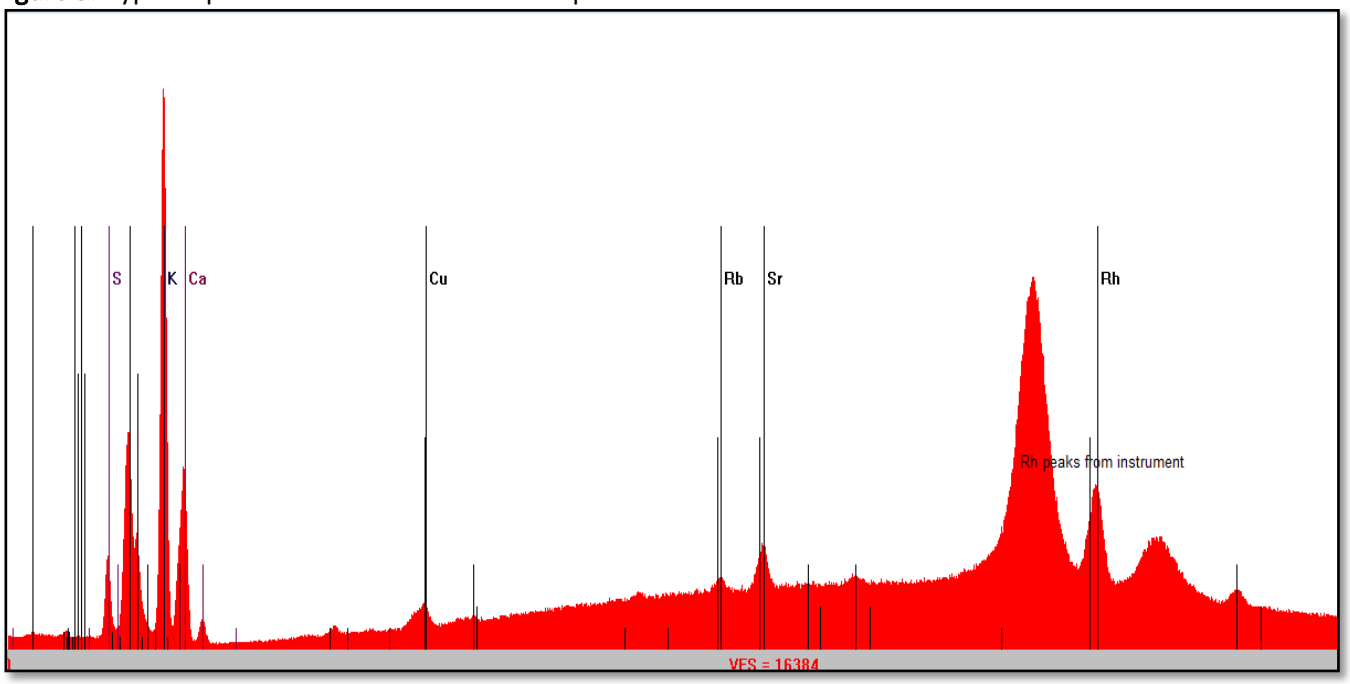

Figure 4: S calibration curve

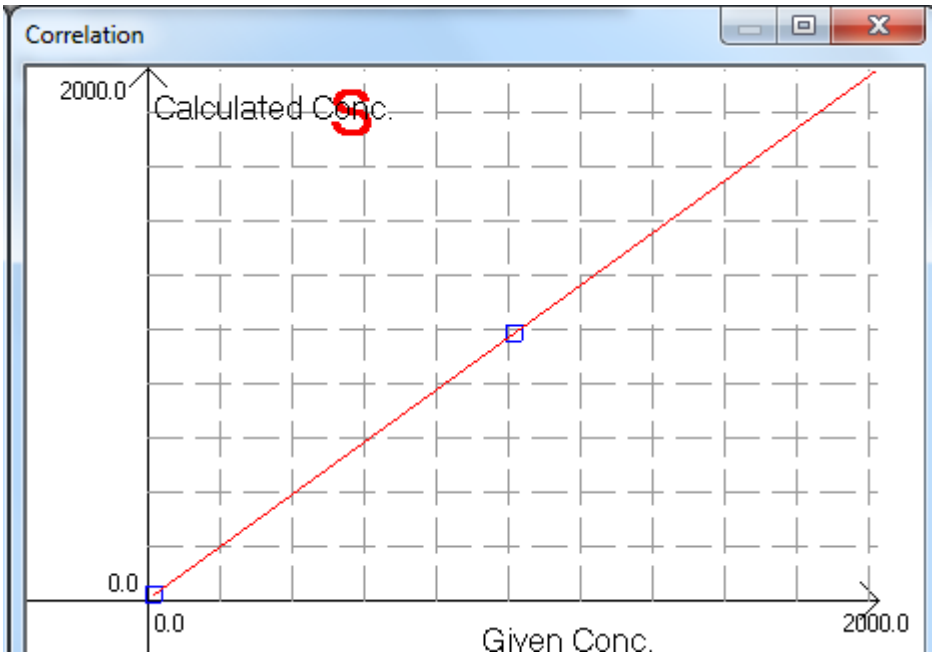

Table 4: Beet Molasses statistic precision test result (N=10)

Element	Mean value [ppm]	standard deviation [ppm]	RSD [%]
S	1551.0	43.5	2.8

Table 5: Beet Molasses sample homogeneity test result

Portion	S Conc. [ppm]
1	1496.6
2	1309.1
3	1584.2
Average [ppm]	1463.3
Standard deviation [ppm]	140.6
RSD [%]	9.61

Cocoa cake sample

Figure 5: typical spectrum of Cocoa Cake sample

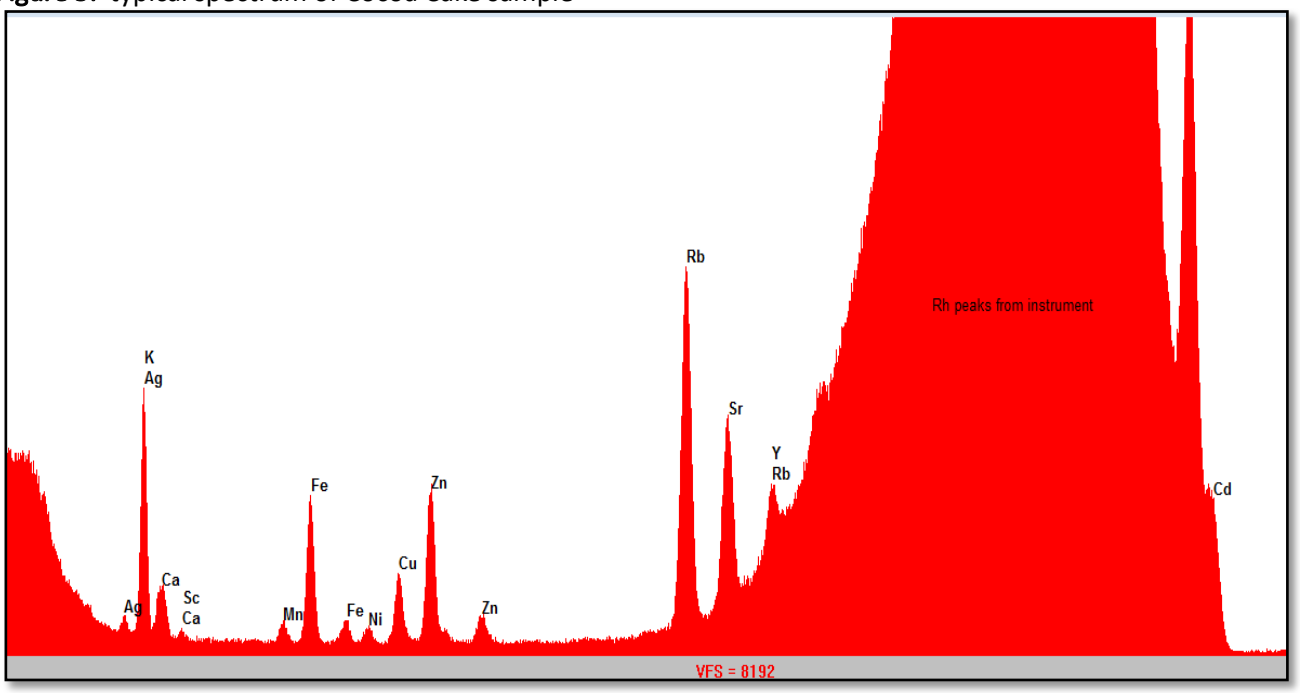

Figure 6: typical spectrum of Cocoa Cake sample showing the Cr peak

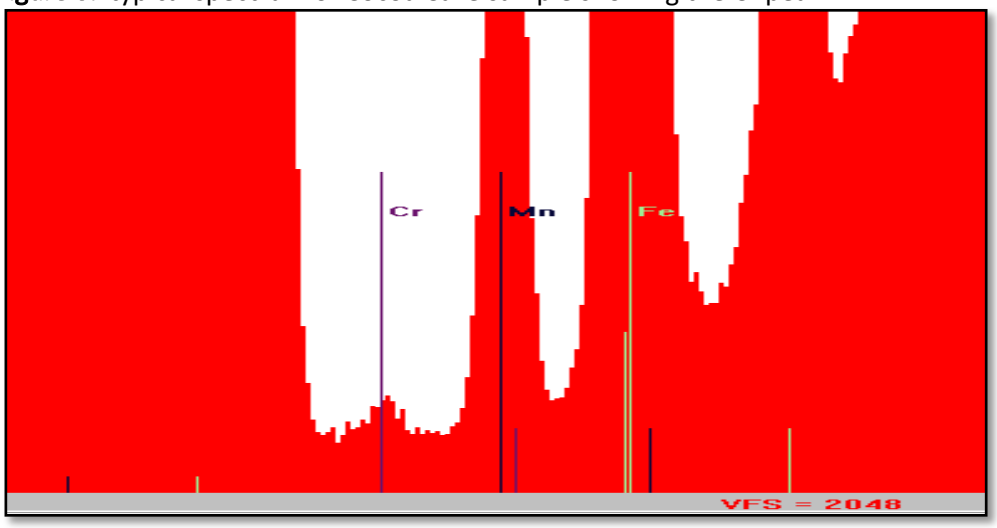

Table 6: Cocoa Cake sample statistic precision test result

Element	Mean value [ppm]	standard deviation [ppm]	RSD [%]
Ni	11.8	1.1	9.3
Zn	80.2	2.2	2.7
Cu	48.0	1.2	2.5
Fe	299.9	5.7	1.9

Table 7: Cocoa Cake sample homogeneity test result

Portion	Ni Conc. [ppm]	Zn Conc. [ppm]	Cu Conc. [ppm]	Fe Conc. [ppm]
1	10.5	77.4	48.9	308.8
2	11.9	76.2	45.1	278.1
3	13.3	75.4	46.8	289.4
Average [ppm]	11.9	76.3	46.9	292.1
Standard deviation [ppm]	1.4	1	1.5	15.5
RSD [%]	12.0	1.3	4.1	5.3

Cocoa mass sample

Cocoa mass sample package include two formats of Coco; stones and powder. Therefore, both sample formats were analyzed.

Figure 7: typical spectra of Cocoa Mass sample; the red maine spectrum is Stone formate and blue contour spectrum is in powder form

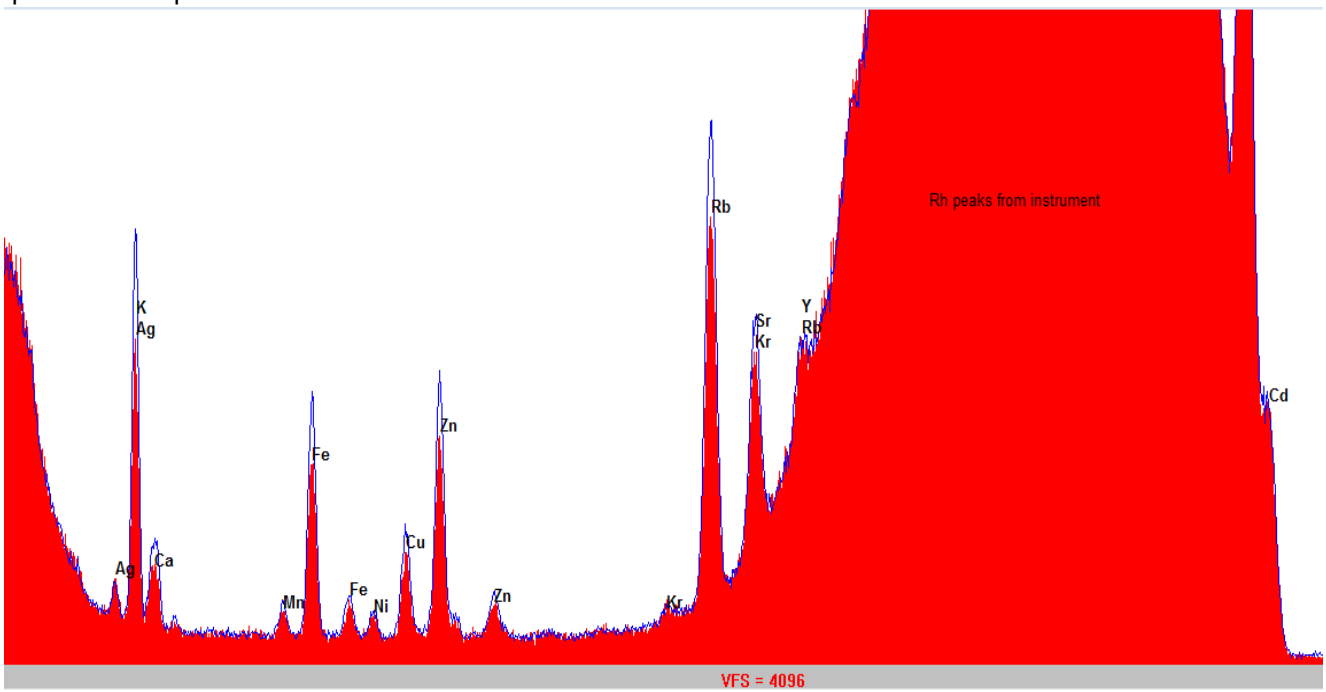

Figure 8: typical spectrum of Cocoa Mass sample showing the Cr peak

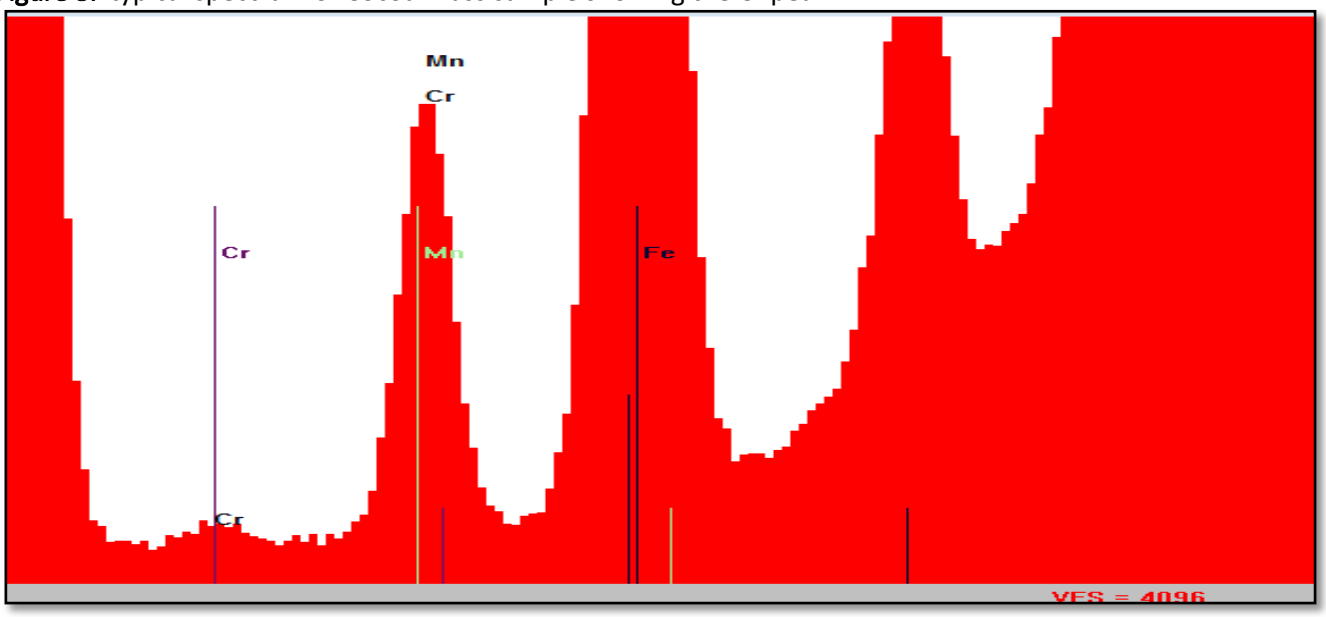

Figure 9: Cocoa Mass spectra; stone format (main red spectrum) and powder format (blue contur) compared to 1000ppm Ni standard spectrum (green contur)

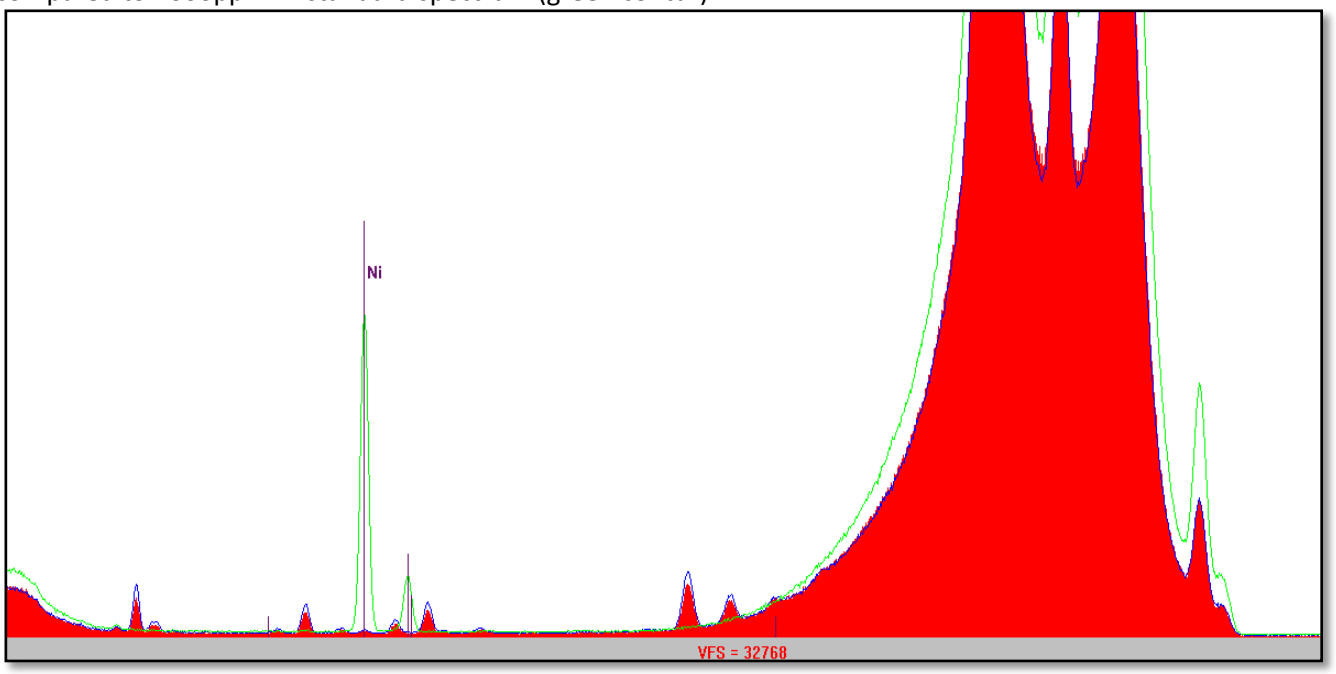

Table 8: Cocoa Mass sample statistic precision test result (N=10 on stone format)

Element	Mean value [ppm]	standard deviation [ppm]	RSD [%]
Ni	7.9	0.8	9.5
Zn	48.9	0.7	1.3
Cu	28.1	1.1	3.8
Fe	199.4	6.7	3.4

Table 9: Cocoa Mass sample homogeneity test results

Portion	Ni Conc. [ppm]	Zn Conc. [ppm]	Cu Conc. [ppm]	Fe Conc. [ppm]
1 (Stone format)	7.7	49.3	28.9	188.5
2 (Stone format)	8.0	48.5	27.0	189.1
3 (Powder format)	11.5	65.5	35.3	265.3
Average [ppm]	9.1	54.4	30.4	214.3
Standard deviation [ppm]	2.1	9.6	4.4	44.2
RSD [%]	23.7	17.6	14.3	20.6

Table 10: Cr content in Cocoa cake and Cocoa Mass samples

Sample	Cr Conc. [ppm]
Cocoa cake	1.3
Cocoa Mass (stone format)	2.1
Cocoa Mass (powder format)	2.5

Conclusions

In conclusion this report shows the excellent use of Xenemetrix EDXRF Analyzer X-Calibur SDD to perform elemental analysis at ppm levels.
Repeatability tests were performed to demonstrate the instrument robustness.
The analysis also provided useful information about the homogeneity of the different received samples.

Comparing Xenemetrix EDXRF analyzer X-Calibur SDD results with the customer expected concentrations show that EDXRF results are accurate although the used references for calibration curves were not the same matrix as Cocoa and Beet Molasses samples.
In general the differences between the matrix of the using standards and the matrix of the samples to be analyzed reduce the accuracy of the quantitative method. However, normalization of the spectrum provided in next software compensates partly for differences in matrix.

Spectrum shown in figure #9 strongly suggest that the Ni content in Cocoa Mass sample is less than 606ppm as measured by other analytic technique.

In summary Xenemetrix EDXRF analyzer X-Calibur is an excellent tool for fast, accurate and reliable measurements on Cocoa and Beet Molasses samples.