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Total reflection X-ray fluorescence as a fast multielemental technique for human placenta sample analysis

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ABSTRACT

In the present contribution, benchtop total reflection X-ray fluorescence spectrometry (TXRF) has been evaluated as a cost-effective multielemental analytical technique for human placenta analysis.
An easy and rapid sample preparation consisting of suspending 50 mg of sample in 1 mL of a Triton 1% solution in deionized water showed to be the most suitable for this kind of samples. However, for comparison purposes, an acidic microwave acidic digestion procedure was also applied. For both sample treatment methodologies, limits of detection for most elements were in the low mg/kg level.
Accurate and precise results were obtained using internal standardization as quantification approach and applying a correction factor to compensate for absorption effects. The correction factor was based on the proportional ratio between the slurry preparation results and those obtained for the analysis of a set of human placenta samples analysed by microwave acidic digestion and ICP-AES analysis. As a study case, the developed TXRF methodology was applied for multielemental analysis (K, Ca, Fe, Cu, Zn, As, Se, Br, Rb and Sr) of several healthy women's placenta samples from two regions in Jamaica.

1. Introduction

The human placenta is a temporary tissue that is formed at the onset of conception. The purpose of placenta is to facilitate the exchange of elements and other substances between the mother and fetus. Therefore, inadequate or excess intake of certain nutrients and toxic elements during pregnancy can affect fetal development [1]. For this reason it is of significance the development of analytical methodologies for multielemental analysis in human placenta samples. High K concentrations in pregnancy (maternal hypotension) have been associated with a low birthweight [2]. Other essential element such as Ca, Br, Fe and Zn are also relevant in human placenta samples. For instance, Zn is considered as one of the key elements in new-born health [3] and Br has been associated with a small but statistically significant increase in risk of birth defects [4]. In addition, the monitoring of toxic elements such as Pb, Cd and Hg has been also performed in this type of biological samples [1].

Commonly used techniques for element determination in placenta samples include atomic absorption spectrometry (with both flame and graphite furnace atomization) [5–6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7] and inductively coupled plasma mass spectrometry (ICP-MS) [8]. This kind of instruments are basically designed for the analysis of liquid samples and thus, biological samples such as placenta have to be brought into solution by means of a wet digestion procedure before the spectroscopic analysis. Although less used, solid state techniques such as neutron activation analysis (NAA) [9,10] and energy dispersive X-ray fluorescence spectrometry (EDXRF) [3,11] have been also employed for multielement analysis of placenta samples.

In the present contribution, for the first time, total reflection X-ray fluorescence spectrometry (TXRF) is proposed for the direct analysis of human placenta samples. TXRF has several advantages over other multielemental spectrometric techniques such as low amount of sample to perform the analysis (μL, μg) and easier quantification by internal standardization (external calibration is not needed). Besides, new low power benchtop TXRF systems are really cost-effective since they do not require gas or cooling media [12].

Most of the papers published so far for direct multielemental analysis of biological samples by TXRF are dealing with the analysis of liquid

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fluids (i.e., amniotic fluid [11], human serum [13] and saliva [14]) but for the analysis of biological solid samples a chemical decomposition is carried out prior to TXRF analysis. In fact, a recent review about sample pretreatment strategies for TXRF analysis highlights that slurry preparation of solid samples (without digestion) accounts only for the 15% of the sample treatment procedures used [15–17]. In the field of human placenta analysis by TXRF, only few scientific contributions have been published and in all of them a previous digestion procedure using nitric acid was performed before TXRF analysis. Moreover, in these studies, large-scaled TXRF systems with high-power X-ray tubes (3 kW) were used [18–19].

The aim of this research was to develop a cost effective and fast method for multielemental analysis of human placenta samples by benchtop TXRF instrumentation. For that, preparation of the sample as slurry was tested as preparation strategy for TXRF analysis. Evaluation of method trueness was performed by comparing the obtained results with those obtained after microwave acidic digestion and further TXRF and ICP-AES analysis. The developed methodology was applied for multielemental analysis of several healthy women's placenta samples from two regions in Jamaica.

2. Experimental section

2.1. Sample collection

A total of twenty placental samples were collected from healthy women in the age group 18 to 42 years in two different parishes in Jamaica, Manchester and St. Andrew. The parish of Manchester is characterized with terra rossa (red limestone) soils, while St. Andrew has mainly rendzinas (black limestone) soils [20]. For this study, ethics approval was granted from the Faculty of Medical Sciences ethics committee at the University of the West Indies. Placental samples were collected from participants of the University of the West Indies (UHWI) in St. Andrew and the Mandeville Regional Hospital in Manchester.

2.2. Sample treatment

The whole placenta was thoroughly examined for any abnormalities. It was washed to remove maternal blood. The weight of the placenta was recorded and approximately, a quarter of the flat part of the placenta from the region of the umbilical cord was severed with a surgical blade. It was then placed in a sealed plastic bag and stored in a freezer at −20 °C. The samples were placed in a drying oven (Memmert, Schwabach, Germany) at 60 °C. The oven was set to maintain a constant temperature for approximately 96 h until a constant dry weight of each placenta was obtained. These dried samples were ground to fine powder for later analysis. Two different sample treatment procedures (digestion and suspension) were tested in order to analyse human placenta samples by TXRF.

2.2.1. Sample digestion

A microwave acid digestion, based on the EPA method 3052, was employed for the preparation of human placenta samples. About of 500 mg of sample was added in PTFE vessel with 8 mL of nitric acid (69%, HIPERPUR, Panreac) and 2 mL of hydrogen peroxide (≥30%, TraceSELECT®, Sigma-Aldrich). The vessels were closed and heated following a two-stage microwave digestion program consisting of a first step of 5 min to reach 180 °C and a second step of 10 min at 180 °C (Ethos Plus Milestone microwave with HPR-1000/10S high pressure rotor (Sorisole, Bergamo, Italy)). After cooling, digested sample solutions were transferred to a 30 mL flask and brought to volume with ultrapure de-ionized water. From each sample digest, an aliquot of 1 mL was fortified with a suitable volume of a Y solution (internal standard) to have a final concentration of 8 mg/L. After that, 5 μL of the internal standardized sample was deposited on a quartz glass reflector and dried using an infrared lamp for the later TXRF analysis.

2.2.2. Sample suspension

A preliminary study was performed to select the most suitable amount of sample and disperser agent to suspend biological samples. According to the obtained results (see Section 3.1 for details), finally, sample suspensions were prepared by weighing 50 mg of sample and adding 1 mL of Triton X-100 1% (v/v) containing 10 μg of Y as internal standard. Duplicates were prepared for each sample. The sample deposition volume and drying mode to perform TXRF analysis were the same as for the digested samples.

2.3. Instrumentation

TXRF analysis of all samples was performed using a benchtop TXRF system (S2 PICOFOX, Bruker AXS Microanalysis GmbH, Berlin, Germany) equipped with a 50 W X-ray tube with a tungsten (W) anode. The characteristic radiation emitted by the elements present in the sample is detected by a silicon drift detector with an active area of 10 mm^2 and a resolution of 147 eV (Mn Kα). The measurements were performed working at 50 kV and 1000 μA and in air environment. Energy values and analytical lines used for TXRF measurements were: K (K_α: 3.314 keV), Ca (K_α: 3.692 keV), Cr (K_α: 5.415 keV), Mn (K_α: 5.900 keV), Fe (K_α: 6.405 keV), Co (K_α: 6.931 keV), Ni (K_α: 7.480 keV), Cu (K_α: 8.046 keV), Zn (K_α: 8.637 keV), As (K_α: 10.543 keV), Se (K_α: 11.224 keV), Br (K_α: 11.924 keV), Rb (K_α: 13.396 keV), Sr (K_α: 14.165 keV), Cd (K_α: 23.173) and Pb (L_α: 10.551 keV).

A stereoscopic optical microscope from (NIKON SMZ-1000) was used for morphological study of sample suspensions deposited on quartz reflectors.

In order to study if elements at ultra-trace concentrations (<1 mg/kg) were present in the target human placenta samples, one of the samples was analysed by synchrotron based TXRF (SR-TXRF) at the IAEA end-station of the XRF beamline at Elettra Sincrotone Trieste [21]. The end-station consists of an ultra-high vacuum chamber that includes as main instrument a seven-axis motorized manipulator for sample and detectors positioning, different kinds of X-ray detectors and optical cameras. The beamline end-station allows performing measurements in different X-ray spectrometry techniques including TXRF measurements [22]. This beamline offers, at its present configuration, tunable SR excitation in the energy range from 3.6 to 14.5 keV by means of a double crystal Si(111) monochromator with a resolving power of 1.4×10^{-4}. The beam size at the sample position is equal to around 260 μm (H) × 130 μm (V) and XRF spectra are acquired by a SDD (Bruker nano GmbH, X-Flash 5030) with a nominal area of 30 mm^2, 450 μm crystal thickness and an energy resolution of 131 eV (FWHM) at the Mn Kα (5.9 keV) line.

For comparison purposes, digested samples were also analysed by means of an Agilent ICP-OES 5100 Synchronous Vertical Dual View (SVDV) spectrometer. Element wavelengths (nm) used were: K (766.491), Ca (422.673), Fe (238.204), Cu (324.754), Zn (213.857), Rb (780.026) and Sr (407.771). The plasma was operated with 12 L/min plasma gas and the plasma configuration elements were: radial (K, Ca) and axial (other elements). The type of detector was silicon based multichannel array CCD (charge coupled device). Other parameters were: 1200 W RF power, concentric nebulizer type and polychromatic wavelength selector.

3. Results and discussion

3.1. TXRF method development

As stated in the Introduction, one of the aims of this contribution was the development of a simple, fast and cost-effective TXRF method for multielemental analysis of human placenta samples. For that,

preparation of the sample as slurry was tested as preparation strategy for TXRF analysis. To perform analysis under total reflection conditions, samples must be provided as thin layers on a reflective carrier. For this reason, the thickness of the deposited sample, is considered as a critical parameter regarding the matrix effects and can really affect the elemental determination. The influence of the amount of biological powder sample as well as the type of dispersing agent used to suspend the sample was studied by analysing the biological certified reference material GBW08571 (Mussel muscle tissue) from the National Research Centre for Certified Reference Materials, Beijing, China. For that, 25, 50 and 100 mg of the reference material GBW08571 were mixed with 1 mL of 1% Triton® X-100 in water and were analysed by TXRF. As it can be seen in Fig. 1A, slightly better results were obtained when preparing the slurry suspending 50 mg of powdered biological material. Using lower or higher amounts of sample a higher dispersion of the obtained results was found, above all for trace elements (Fig. 1A).

The type of dispersing agent used to prepare the suspension is also an important parameter to be tested. Some contributions have shown that the homogeneity of the suspension can be improved if using a surfactant solution to prepare the suspension [15]. In view of these previous findings, in the present contribution, bidistilled water and a dilution of 1% Triton X-100 in de-ionized water were tested as dispersing agents to prepare the biological suspensions. Moreover, in addition to compare the quantitative results obtained using the different dispersant agents (Fig. 1B) we performed a morphological study of the deposited drop on the reflector to study in more detail the homogeneity of the analysed sample. The morphological study was performed using a stereoscopic optical microscope in transmitted light to check the homogeneity of the sample spot. In Fig. 2 the images obtained for a 10 μL sample spot in quartz glass reflector for each type of solution used to prepare the suspensions are shown. For comparison purposes, in addition to the biological reference material GBW08571, a real human placenta sample was considered. From the obtained optical microscope images, it can be seen that a similar homogeneity of the sample drop was obtained for both the biological CRM and the human placenta sample using bidistilled water and a 1% Triton X-100 solution. The only relevant difference was the diameter of the sample spot on the sample that was higher when using 1% Triton X-100 solution and thus the thickness of the deposited sample was lower in comparison with the use of bidistilled water to suspend the biological material. Taking into account this fact and the slightly better quantitative results obtained when using a solution of 1% Triton X-100 to suspend the sample, this disperser agent was selected for the preparation of the human placenta samples.

Regarding the sample deposition on the reflector to perform the TXRF analysis, a volume of 5 μL was established since using this volume the sample was provided as a centred-thin film on the reflector.

Operating conditions for TXRF measurements were also evaluated. The rate of kV/mA of the X-ray tube was selected to work under conditions of maximum efficiency of excitation (50 kV, 1 mA, max. power 50 W). The effect of measuring time on the uncertainty of the obtained results was also evaluated by analysing five replicate samples of the certified material GBW08571 at different measuring times (500, 1000, 2000 and 3000 s). For minor elements, a measuring time of 1000 s was enough to obtain a relative standard deviation of the results lower than 5%. However, for elements present at lower concentrations (<1 mg/kg), a significant reduction of the RSD values was achieved when using longer measurement times. Taking into account that the aim of the study was the development of a multielemental method (including minor, trace and ultratrace elements), a measuring time of 3000 s was finally selected for further TXRF analysis.

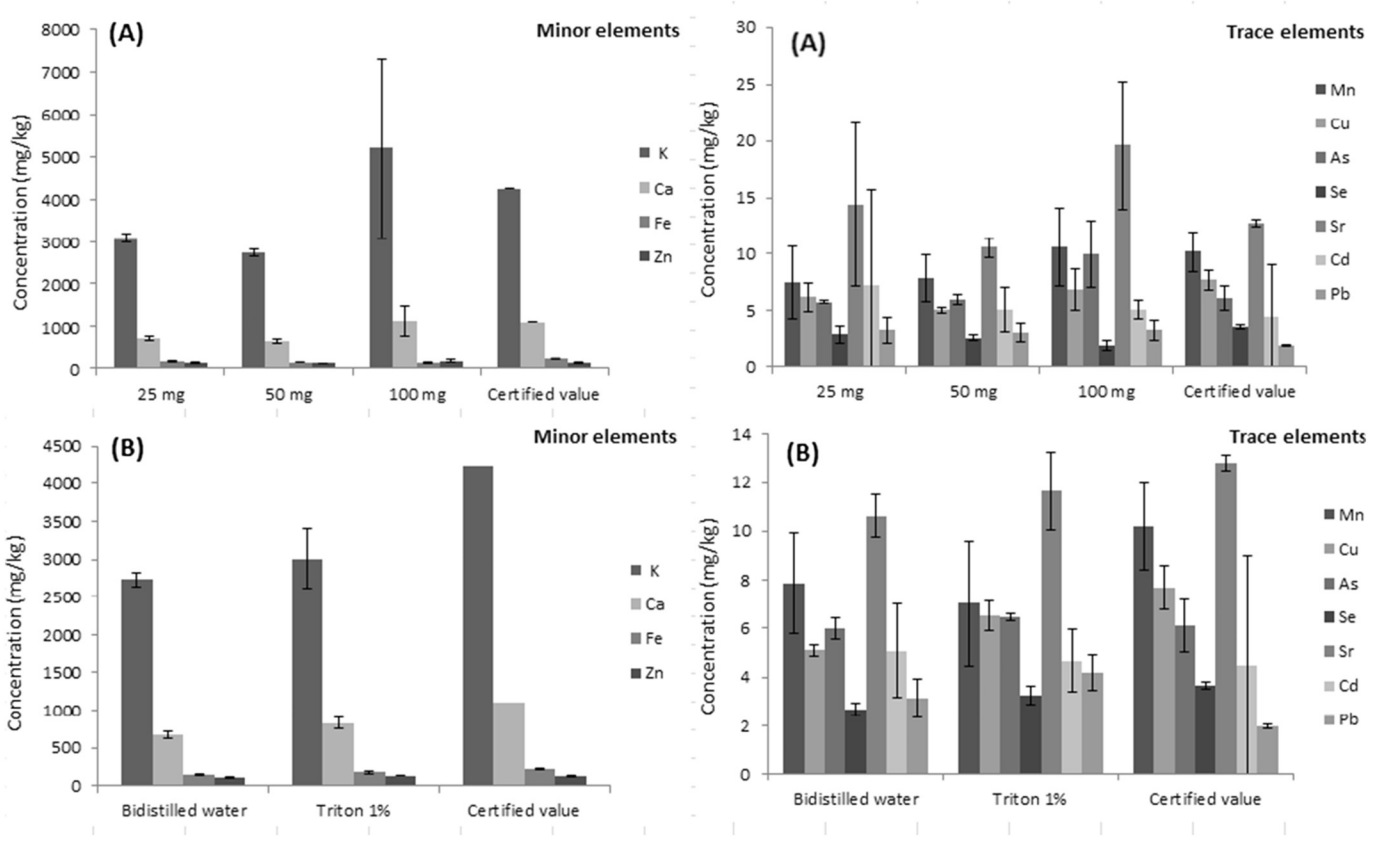

Fig. 1. Effect of suspension preparation on measured element content by TXRF analysis: (A) Effect of sample amount (disperser agent: Triton 1% solution), and (B) effect of disperser agent type (sample amount: 50 mg). Tests were performed using the certified reference material GBW08571 (Mussel muscle tissue). Error bars represent standard deviation of duplicate samples.

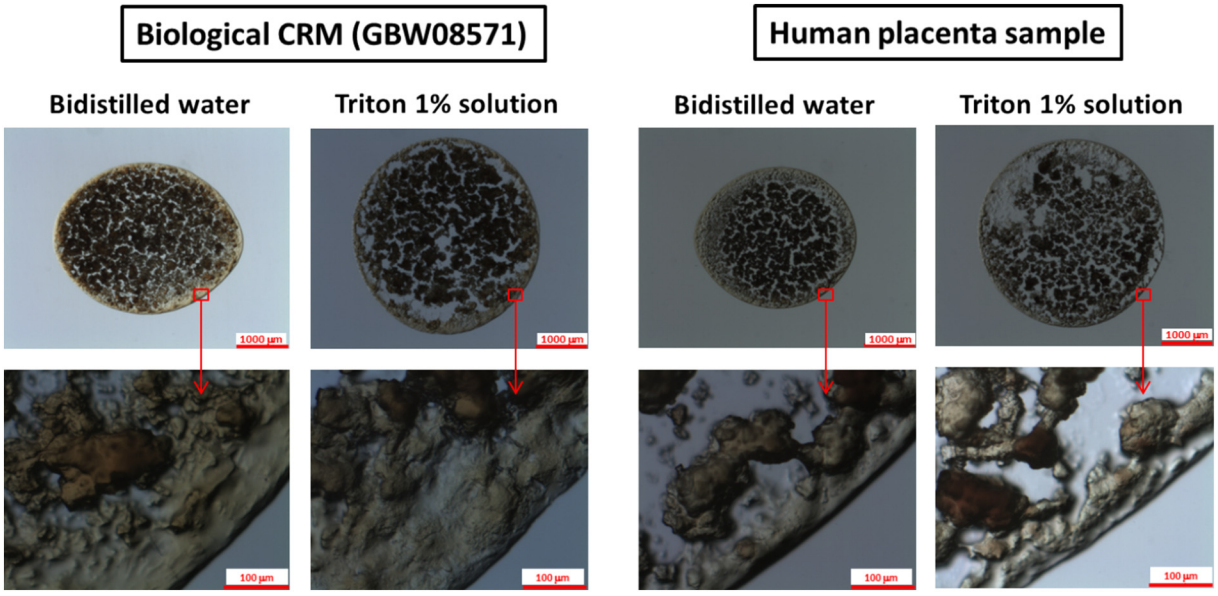

Fig. 2. Optical microscope images in transmitted light for a 10 µL sample spot in quartz glass reflector prepared by suspending 50 mg of the biological sample (CRM GBW08571 and human placenta) using bidistilled water and Triton X-100 (1%).

3.2. Analytical figures of merit of the TXRF method

Limits of detection (calculated using the 3σ definition [23]) and accuracy of the results, using the preparation of a suspension of the biological reference material for subsequent TXRF analysis, were compared with those obtained when using a more sophisticated sample treatment based on a microwave acidic digestion (see details in Section 2.2.1). Obtained results are summarized in Table 1. As it can be seen, the limits of detection for most elements are similar using both sample treatments (low mg/kg range). Only for some specific elements such as Cd, K and Ca the limits of detection are slightly lower using MW digestion. Regarding the accuracy of the obtained results, in most cases, recovery values were acceptable (85–100%) even when using the simpler sample preparation procedure (slurry preparation). From the obtained results, it can be deduced that the slurry preparation in combination with TXRF can be a powerful analytical tool to get multielement information in a simple and fast way. However, for the determination of toxic elements such as Pb more sophisticated sample treatment procedures in combination with more sensitive techniques are needed since the quantification of these elements in the low mg/kg range is not reliable. Global precision of the developed methodology (slurry preparation) was also tested by analysing four independent replicates of the same certified reference material mentioned above. Besides, one of the replicates was measured four times and the relative standard deviation (RSD) associated was also calculated. This uncertainty is related to the instrument stability and counting statistics. Therefore, by means of error propagation, the total uncertainty including sample preparation can also be estimated. Results are displayed in Fig. 3. As it is shown, global precision is acceptable for minor and trace elements with RSD values of 6.2 and 13.3%, respectively. On the contrary, a poor precision is obtained for element determination at ultratrace levels (RSD ~ 88%) due to the proximity to the detection limits (see Table 1 for details). From Fig. 3 it can also be deduced that instrument uncertainty has a significant contribution (~50%) to the global precision of the obtained results at trace and ultratrace concentration levels.

3.3. Analysis of human placenta samples by slurry preparation and TXRF analysis

A first test was carried out in order to study the quality of the TXRF results obtained for the analysis of human placenta samples. For that, one of the human placenta samples was analysed by TXRF (slurry and MW digestion sample preparations) and results were compared with those obtained after MW digestion and ICP-OES analysis. As it is shown in Table 2, for most elements, good agreement was obtained when comparing results by TXRF and ICP-OES after MW digestion.

Table 1
Limits of detection and results obtained for the analysis of the reference material GBW08571 (mussel muscle tissue) using suspension preparation or MW digestion before TXRF analysis. Results are expressed in mg/kg as the mean with the associated standard deviation (mean ± SD, $n = 2$).

Element	Limits of detection		Mussel muscle tissue (GBW08571)		
	Suspension	Digestion	Suspension	Digestion	Certified
K	58	41	3000 ± 400	2700 ± 400	(4240)
Ca	41	25	830 ± 70	900 ± 100	(1100)
Fe	3.6	3.3	180 ± 20	186 ± 7	221 ± 14
Zn	1.3	1.4	134 ± 3	135 ± 5	138 ± 9
Cu	1.6	1.0	6.5 ± 0.5	11 ± 2	7.7 ± 0.9
As	0.8	1.5	6.5 ± 0.2	5 ± 2	6.1 ± 1.1
Se	1.0	1	3.3 ± 0.4	3.2 ± 0.3	3.65 ± 0.17
Sr	0.8	0.6	12 ± 2	16 ± 1	12.8 ± 0.32
Cd	1.3	0.6	5 ± 1	4.1 ± 0.1	4.5 ± 4.5
Pb	0.5	0.5	4.2 ± 0.7	3 ± 1	1.96 ± 0.09

Indicative values are presented in brackets.

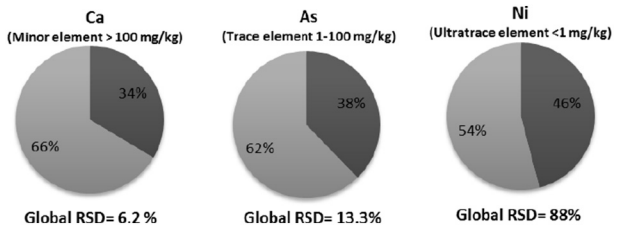

Fig. 3. Contribution to the global precision of the results ($n = 4$). Legend: Dark grey (instrument uncertainty), light grey (sample preparation uncertainty).

Larger discrepancies were found for light elements such as K and Ca. However, a systematic underestimation of the concentration values (up to 65%) was obtained when comparing TXRF by slurry preparation and ICP-OES analysis. It seems that the thin film approximation for this type of samples and analytical conditions is overestimated and therefore absorption effects cannot be considered negligible. In order to cope with this fact, a correction factor was applied to slurry preparation results. The correction factor was based on the proportional ratio between the slurry preparation results and those obtained for the analysis of ten human placenta samples by ICP-AES. Relative standard deviation of the estimated correlation factors was between 5 and 15%. This practice has been already applied in many field portable XRF analysis methods [24]. A theoretical estimation of the correction due to the absorption effects further confirmed its importance and magnitude. An approximate factor of about two was deduced based on the formalism presented by Zarkadas et al. [25], using the mass attenuation coefficients for an equivalent biological matrix (NIST soft-tissue matrix, ICRU-44 [26]) and an estimated areal density for the dry residue equal to 1.5 mg/cm^2. As it can be seen in Table 2, no significant differences at 95% confidence level were obtained between corrected slurry preparation and ICP-OES results and therefore, slurry TXRF results were corrected in further analysis.

In order to study if other elements at ultra-trace concentrations (<1 mg/kg) were present in the target human placenta samples, one of the samples was analysed by synchrotron based TXRF (SR-TXRF). Synchrotron produced X-ray beams are characterized by high intensity, monochromaticity and high degree of polarization that lead to a significant improvement of detection limits in comparison to conventional X-ray tube systems [21]. In Fig. 4, TXRF spectrum obtained in the XRF IAEA beamline end-station at Elettra Sincrotone (Trieste) [22] is displayed. As it is shown, in addition to other elements already determined by conventional TXRF, only small traces of Ni and Se were detected (at 0.34 and 1.2 mg/kg, respectively). No other toxic elements such as Cr and As were present in the target human placenta sample.

In Fig. 5, results from the multielemental analysis of human placenta samples from two different Jamaica regions using the developed methodology (slurry + TXRF analysis) are presented. Potassium concentration in St. Andrew was significantly higher than in Manchester group. This is possibly due to the higher levels of potassium in St. Andrew soils [27].

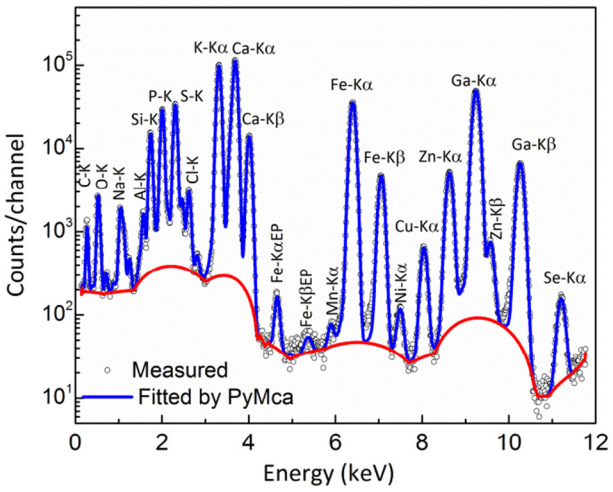

Fig. 4. SR-TXRF spectrum (IAEA end-station of the XRF beamline at Elettra Sincrotrone Trieste) for a digested placenta sample (HP067). Excitation energy: 13.0 keV. In red: background correction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Regarding minor elements (>100 mg/kg), no significance differences were obtained between K and Fe content in the studied Jamaica locations (RSD values ~14%). On the contrary, Ca content presents a significant variability between the two regions studied but also within the same region with RSD values between 85 and 100%. A similar trend is found for Br content in placenta samples collected in Manchester region where its concentration varies in the range from 7 to 54 mg/kg and it is slightly higher in comparison with St. Andrew samples. This fact possibly reflects the elevated levels of this element in the lateritic rich-bauxite soil environment. Other trace elements studied (Zn, Rb, Cu, As, Se and Sr) are distributed rather homogeneously among the human placenta samples and not significantly differences are found between the studied regions. The elemental concentrations obtained for the study group in Jamaica are in good agreement with similar studies carried out in other countries [11].

It is interesting to remark that in sample HP004 (St. Andrew region) the Cr concentration (36 ± 1 mg/kg) was much higher compared to the other placenta samples. This value was confirmed also by analysing the same sample by MW digestion and ICP-OES (37 ± 2 mg/kg). Similar value was obtained as well as by EDXRF analysis using Niton XL3T GOLDD analyser. Additional samples should be measured from this region in order to understand if the elevated Cr amount is due to dietary habits or environmental conditions.

4. Conclusions

In this work we have demonstrated the possibilities of low power TXRF spectrometry for multielemental analysis of human placenta samples. The use of direct analysis of placenta sample suspensions could be

Table 2
Results obtained for the analysis of the placenta sample (HP067) using different analytical methodologies. Results are expressed in mg/kg as the mean with the associated standard deviation (mean ± SD, $n = 2$).

Element	TXRF (suspension)	TXRF (suspension corrected)[a]	TXRF (MW digestion)	ICP-OES (MW digestion)
K	5200 ± 400	9000 ± 800	5300 ± 30	8690 ± 50
Ca	3250 ± 40	7060 ± 90	5500 ± 200	7650 ± 80
Fe	390 ± 30	600 ± 50	564 ± 5	600 ± 90
Cu	4.0 ± 0.3	5.4 ± 0.4	5.59 ± 0.03	6.1 ± 0.7
Zn	35 ± 2	55 ± 4	49 ± 1	51 ± 2
Rb	9.3 ± 0.7	8.7 ± 0.7	8.2 ± 0.4	8.5 ± 2

[a] Corrected values (see manuscript text for details).

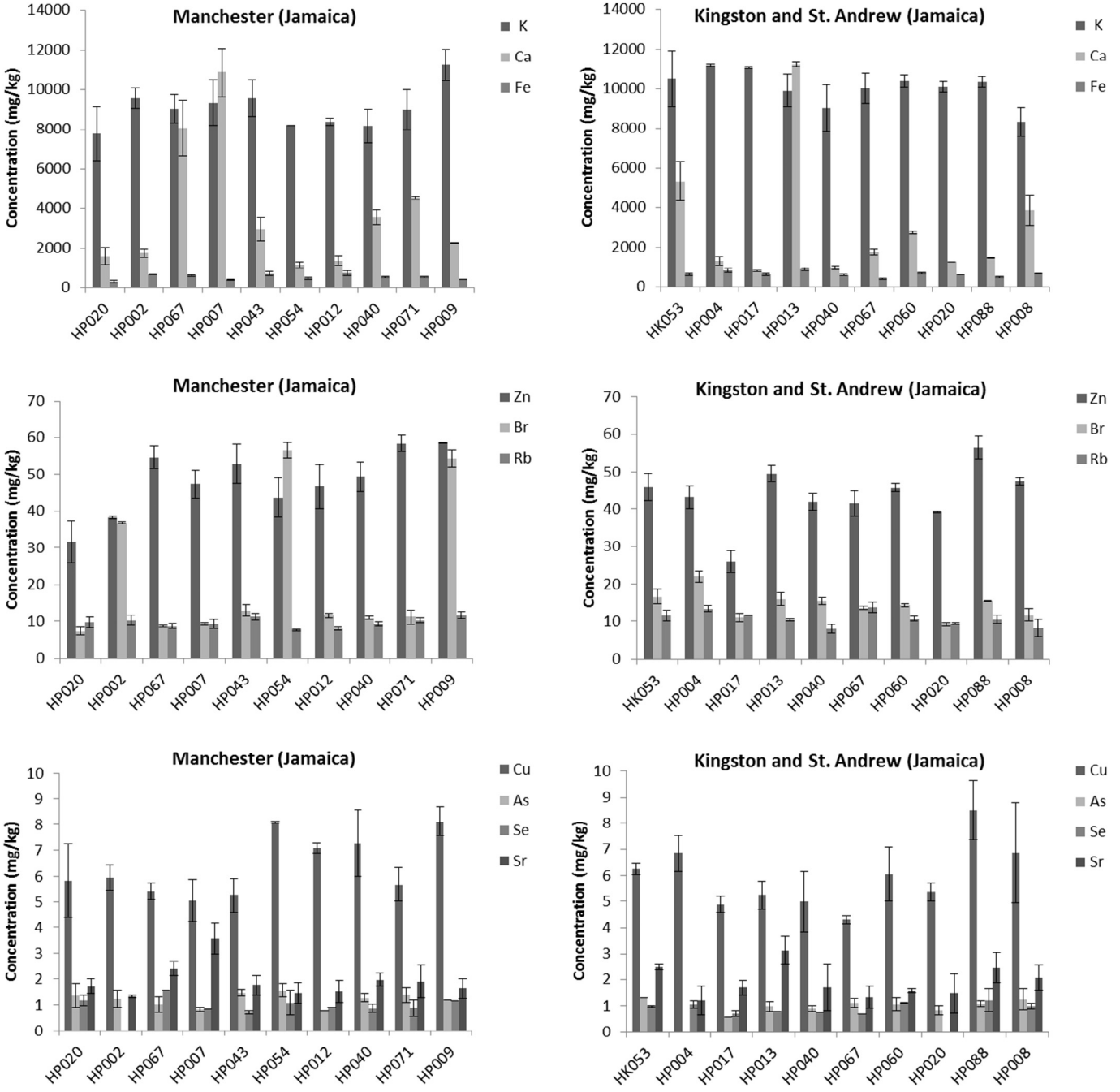

Fig. 5. Multielemental analysis of human placenta samples from different Jamaica regions (analytical procedure: slurry + TXRF analysis). Error bars represent standard deviation of duplicate samples.

interesting as a fast and relatively simple methodology to get quantitative information on minor and trace element content in this kind of samples. However, for the determination of toxic elements such as Pb and Cd, present at ultra-trace levels, more sophisticated sample treatments as well as more sensitive techniques are needed. Obtained results from the analysis of the target human placenta samples revealed that most minor and trace elements are homogeneously present and not significantly differences were found between the studied regions. The only exceptions were Ca and Br which present a high variability between the two regions studied but also within the specimens from the same region. Additional studies are needed to find out if this variability can be related to environmental exposure of both mother and fetus.

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