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Comparison of analytical performance of benchtop and handheld energy dispersive X-ray fluorescence systems for the direct analysis of plant materials

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Abstract

The analytical performances of benchtop and handheld energy dispersive X-ray fluorescence spectrometry (EDXRF) systems were evaluated aiming at the direct and simultaneous determination of P, K, Ca, S, Fe, Mn, and Si in plant materials. Pressed pellets of comminuted leaves from 23 varieties of sugar cane were used as laboratory samples. Both systems presented similar figures of merit, and were able to provide useful data for plant nutrition diagnosis. Linear correlation between the elemental mass fractions in the test samples and characteristic X-ray intensities were obtained for all analytes with both equipments. Correlation coefficients from 0.9601 to 0.9918 and from 0.9094 to 0.9948 were attained for benchtop and handheld EDXRF, respectively. The coefficient of variation of measurements carried out in 3 different test samples were also appropriate, being lower than 13 % for all analytes. Limits of detection were comparable for both systems (20 mg kg^{-1} for Fe and Mn, and approximately 0.1 g kg^{-1} for P, K, Ca, S and Si) and permit the evaluation of the mineral nutrition status of sugar cane crop taking into account the critical levels of these elements. Handheld system is a cost-effective and appealing option for those who intend to carry out faster *in situ* and laboratory analysis with equivalent performance of the benchtop equipment.

Keywords

X-ray fluorescence spectrometry, macronutrients, micronutrients, silicon, sugar cane, portable XRF.

Introduction

Foliar diagnosis aiming at the evaluation of plant nutrition status has been successfully used by providing reliable data on nutrient crop requirements and potential deficiencies.[1-3] The first evidence of malnutrition is often recognized *in situ*, through visual identification of symptoms. For a more detailed evaluation, leaf mineral analysis is highly recommended, which enables a more effective fertilization program.[4]

With the advent of instrumental methods of analysis, notably after the consolidation of inductively coupled plasma optical emission spectrometry (ICP OES), simultaneous determination of P, K, Ca, Mg, S, Fe, Cu, Mn, Zn and B in acid digests became possible.[1] These essential elements can be measured in just 30 s spending one-mL of liquid sample by using modern axial- or radial-viewed ICP optical emission spectrometers.[1] However, to accomplish this purpose, plant materials must be converted to an appropriate solution, which is normally carried out by microwave-assisted acid digestion.[5-6]

Recently, attempts towards Green Chemistry have led to the proposal of methods based on direct analysis of solids.[7] Regarding plant materials, the sample, generally in powder form, can be analyzed by *e.g.* X-ray fluorescence spectrometry (XRF),[8-11] laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS),[12-15] laser-induced breakdown spectroscopy (LIBS)[16-19] and electrothermal vaporization ICP OES (ETV-ICP OES).[20-21]

Wavelength-dispersive X-ray fluorescence (WDXRF) and energy-dispersive X-ray fluorescence (EDXRF) methods allow the unequivocal identification of an element, as its concentration is estimated by the characteristic X-ray emission intensity. EDXRF systems are currently one of the most widespread used XRF method for routine analysis owing to its simple optical arrangement, fast analysis time, as well as low purchase and running costs.[22-23] The EDXRF system based on three-axial geometry (the X-ray tube, the sample and the secondary target are in a 3-D design) is a good alternative to achieve better limits of detection, as the spectrum background can be reduced by one order of magnitude in relation to the spectrometers with direct source-sample (2-D) geometry.[24-26] Scanning Electron Microscopy (SEM) is a possible alternative for atomic excitation by focusing an electron beam onto the sample, and the elemental information being acquired by coupling it with an energy dispersive detector.[27] The SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy) can be used for the determination of low atomic number elements with X-ray characteristic energy below 2 keV[28] such as nitrogen, whose limit of detection is approximately 5 g kg^{-1}. [29] However, SEM-EDS requires electrically conductive test samples; otherwise a sample pre-treatment step will be needed.[30] In addition, the instrumentation cost is higher than EDXRF spectrometers.

Benchtop EDXRF systems have presently received increasingly attention due to the higher performance of the available equipments. Modern spectrometers offer several advantages to the analyst as automated analysis, spectral deconvolution and fundamental parameter algorithms. Furthermore, these equipments have special chambers designed to operate under air, vacuum or helium atmosphere.[22]

In the last 20 years, advances in X-ray spectrometry have lead to pronounced improvements in the instrument analytical capabilities. The development of miniature X-ray tube to replace the less safe radioactive isotope source was a successful insight. This trend was followed by the construction of mobile devices opening up attractive possibilities of studies.[31]

Portable XRF (PXRF) instruments present some benefits over the benchtop systems such as the simplicity of operation, the possibility of *in situ* investigations and analysis of large samples.[32-34] Moreover, the operational costs of modern PXRF instruments are considerably lower when compared to typical benchtop laboratory units.[35] In addition, an interesting outspread of this technology is the possibility to present the spectrometer to the sample in field analysis.[36]

In spite of its analytical capabilities and suitable performance for several applications, PXRF measurements may suffer from low sensitivity for low atomic number elements because low energy fluorescent X-rays are attenuated by the air atmosphere. To circumvent this drawback, some instruments provide a partial vacuum device.[32] Alternatively, the measurements can be carried out under helium atmosphere as described by Reidinger et al.[35] and McLaren et al.[37] in the analysis of plant materials using PXRF systems.

Analytical applications of benchtop EDXRF systems for elemental analysis of plant materials are experiencing a fast growth. A myriad of vegetal matrices such as coffee,[8] sugar cane,[9] rice,[23, 38] barley,[39] pearl millet,[23] spice,[40] tobacco,[41-42] wheat,[43] sorghum,[44] tea,[45-46] , medicinal plants,[47-50] tropical fruits,[51] and others[10, 52-54] have been investigated in these studies.

To the best of the authors' knowledge, there is no study comparing the performance of benchtop and portable EDXRF equipments for the analysis of plant materials. The aim of this work was therefore to critically evaluate and compare the performances of a benchtop and handheld EDXRF systems for the direct determination of nutrients and beneficial elements in pressed pellets of plant materials. In this sense, both equipments were operated under optimal conditions aiming at the simultaneous determination of the target analytes. The main figures of merit, as limit of detection, linearity, Prediction Error Sum of Squares (PRESS), Root Mean Square Error of

Prediction (RMSEP), precision, and analytical throughput were taken into account for method validation.

Materials and Methods

Samples

Sugar cane leaves from 23 varieties were collected in Piracicaba, SP, Brazil, according to the procedure described by McCray et al.[55] This sampling protocol prescribes the collection of the Top Visible Dewlap (TVD) leaf, which is the uppermost fully expanded leaf that has a distinguished collar.[55] Elemental concentration of the TVD leaf provides a snapshot diagnosis about the nutritional status of plants.[55] The following sugar cane varieties were used as laboratory samples: CTC1 to CTC18, IAC 85-5433, RB 86-7515, IAC 87-3396, IAC 93-6006 and IAC 81-3250. After sampling, leaf blades were washed with deionized water and the midrib was manually detached. Samples were placed in clean paper bags and dried at 60 °C until constant weight. Thereafter, the dried leaves were ground in a Wiley type knife mill and further comminuted in a cryogenic mill (Spex model 6800, USA) as described elsewhere.[56] Pellets were prepared, in triplicate, in a Spex model 3624B X-Press by transferring 0.5 g of comminuted material to a 15 mm internal diameter stainless steel die set and applying 8.0 t cm^{-2} for five min obtaining cylindrical pellets of approximately 2 mm thickness.

Reference methods for EDXRF calibration and validation

A microwave-assisted acid digestion[56] was carried out in triplicate in closed TFM® vessels (ETHOS 1600, Milestone, Italy), for the determination of P, K, Ca, S, Fe and Mn by ICP OES. The cryogenically ground plant material was accurately weighed (*ca.* 250 mg), transferred to the digestion vessels and 6.0 mL of 2.8 mol L^{-1} HNO_3 and 2.0 mL of H_2O_2 30 % w/w were added. The microwave heating program was selected as follows: step 1: room temperature to 120 ºC with a ramp of 3 min; step 2: 2 min at 120 ºC; step 3: 120 °C to 160 ºC with a ramp of 4 min; step 4: 160 °C to 220 ºC with a ramp of 5 min; step 5: 15 min at 220 ºC. After cooling, the final solutions were transferred to volumetric flasks and diluted up to 25 mL with deionized water.

For Si determination, an oven-induced alkaline digestion[57] was selected, according to reference method for Si determination in sugar cane leaves. In this procedure, 100 mg of cryogenically ground plant material were accurately weighed in triplicate and transferred to 50.0 mL polyethylene tubes, previously rinsed with 0.1 mol L^{-1} NaOH and deionized water. Octyl alcohol (five drops) was added as an antifoaming agent. Afterwards, 2.0 mL of 30 % w/w H_2O_2 was added. The tubes were capped and placed in a convection oven at 95 ºC. The tubes were removed after 30 min heating, and 4.0 mL of a 50 % w/v NaOH solution was added. The tubes were manually shaken, capped and placed in the oven at 95 ºC. After 4 h, they were removed and 1.0 mL of a 5.0 x 10^{-3} mol L^{-1} NH_4F solution was added. The final solutions were diluted up to 50.0 mL with deionized water.

The elemental determinations were performed by using a radially-viewed ICP optical emission spectrometer (Vista RL, Varian, Australia) furnished with a cyclonic spray chamber and a V-groove nebulizer. ICP OES measurement conditions are described elsewhere.[9] The following emission lines were monitored: P I 213.618 nm, K I 769.897 nm, Ca I 422.673 nm, S I 181.972 nm, Fe II 234.350 nm, Mn II 259.373 nm, and Si I 250.690 nm.

Five certified reference materials were also analyzed to check the accuracy of the microwave-assisted acid digestion and ICP OES determination: Apple Leaves

(NIST SRM 1515), Peach Leaves (NIST SRM 1547), Trace Elements in Spinach Leaves (NIST SRM 1570a), Tomato Leaves (NIST SRM 1573a) and Trace Elements in Pine Needles (NIST SRM 1575a). GBW 07603 was also used to check the accuracy of Si determination.

EDXRF instrumentation and measurement conditions

The benchtop unit was an energy dispersive X-ray fluorescence spectrometer EDX-720 (Shimadzu, Kyoto, Japan) fitted with a 50 W Rh target X-ray tube and a Si(Li) semiconductor detector. The system has 16-sample turret positioned inside of a chamber specially designed for analysis under air, vacuum or helium atmosphere. Furthermore, the system permits the switching between four spot sizes (1, 3, 5 and 10 mm diameter).

The handheld instrument was a compact (2 kg, 30 cm long x 10 cm wide x 28 cm height) Tracer III-SD model (Bruker AXS, Madison, USA), equipped with a 2 W Rh target X-ray tube and 10 mm^2 X-Flash® Peltier-cooled Silicon Drift Detector (SDD), and furnished with a portable vacuum pump which achieves pressures lower than 5 torr. Both an acrylic stand and a metal enclosure radiation shield, from the same manufacturer, were used.

The handheld and benchtop EDXRF systems used herein are furnished with Rh target X-ray tubes, which is the only commercially available option.

The operating conditions using both handheld and benchtop EDXRF instruments are presented in Table 1.

Evaluation of calibration models

Two statistical parameters, PRESS and RMSEP were estimated by using the calibration models obtained for all analytes by plotting the mass fractions determined by ICP OES *versus* the corresponding characteristic X-ray emission intensities obtained with each EDXRF system. The PRESS statistics, originally proposed by Allen,[58] was used as follows:

$$\mathrm{PRESS} = \sum \left(y_i - \hat{y}_i\right)^2$$

where yi is the elemental concentration determined by ICP OES and ŷi is the concentration predicted by the model. In addition, RMSEP data were estimated by taking into account the obtained PRESS values:

$$\mathrm{RMSEP} = \sqrt{\frac{\mathrm{PRESS}}{\mathrm{n}}}$$

where n is the number of analyzed sugar cane pellets. In the present investigation, n = 23.

Limit of detection of handheld and benchtop EDXRF methods

The limit of detection (LOD) was estimated by taking into account the background data of the Kα peaks obtained through the deconvolution procedure using the equipment software. Background values of ten different test samples (CTC1 to CTC10) were grouped, and the standard deviation was estimated.

Results and Discussion

Preliminary analysis using benchtop and handheld EDXRF

As an initial evaluation of the analytical capabilities of benchtop and handheld EDXRF systems, a randomly chosen pressed pellet of sugar cane leaves was analyzed using both instruments. The selected sample (CTC 17) presents the following elemental composition obtained with ICP OES determination after wet-based decomposition: (1.46 ± 0.02) g kg^{-1} P, (13.7 ± 0.3) g kg^{-1} K, (3.90 ± 0.10) g kg^{-1} Ca, (1.37 ± 0.04) g kg^{-1} S, (172 ± 6) mg kg^{-1} Fe, (3.84 ± 0.14) mg kg^{-1} Cu, (59.5 ± 0.2) mg kg^{-1} Mn, (15.0 ± 0.4) mg kg^{-1} Zn, and (6.5 ± 0.3) g kg^{-1} Si.

Analysis of the spectra obtained by both benchtop and handheld EDXRF systems (Fig. 1) reveals that it is possible to identify the following peaks: P Kα 2.01 keV, K Kα 3.31 keV, Ca Kα 3.69 keV, Ca Kβ 4.01 keV, S Kα 2.31 keV, Fe Kα 6.40 keV, Mn Kα 5.90 keV and Si Kα 1.74 keV. Most of the samples presented copper (Kα 8.05 keV) and zinc (Kα 8.64 keV) mass fractions near or even below the estimated limits of quantification of 7 mg kg^{-1} Cu and 12 mg kg^{-1} Zn.

For all elements, the signal-to-background ratios (SBR) obtained with both equipments were equivalent. The SBR values of the Kα peaks in CTC 17 varied from 0.34 for Mn to 10 for K for the benchtop EDXRF, and from 0.34 for Mn to 8.5 for K for the handheld unit, and the SBR for the remaining analytes were of comparable magnitudes.

It must be also pointed out that, under the experimental conditions of this work, the detection of Mg Kα 1.25 keV was not possible in view of the low fluorescence yield (2.9 %)[59] and due to its occurrence in plant leaves (1-10 g kg^{-1}).[60]

Experiments were then carried out towards the quantification of P, K, Ca, S, Fe, Mn and Si in the pellets of sugar cane leaves by using all the 23 varieties.

Validation of reference methods for P, K, Ca, S, Fe, Mn and Si determinations

The analysis of the corresponding acid digests of certified reference materials from NIST (SRMs 1515, 1547, 1570a, 1573a, and 1575a) showed that, by applying the

Student's *t*-test at 95 % confidence level, there were no significant differences between certified P, K, Ca, S, Fe and Mn mass fractions and the results obtained by ICP OES. The CRM GBW 07603 was analyzed after alkaline decomposition and the result for Si was in statistical agreement as well.

Selection of X-Ray spot size

The benchtop instrument permits the selection of 1, 3, 5 or 10 mm X-ray spot sizes. A prior optimization of this parameter is of importance for sampling and analytical performance. Best condition was attained when 5 mm beam diameter was selected taking into account the signal-to-noise ratios from the Kα peaks of the abovementioned analytes using the NIST SRM 1515.

Regarding the handheld spectrometer, the user can choose from 3 to 1 mm X-ray spot sizes, and the standard 3 mm beam diameter was selected to provide a better comparison between both equipments in terms of similar analyzed test portions. In addition, selection of higher X-ray spot sizes tends to minimize the errors related to the micro-heterogeneity of the test sample.

Optimization of EDXRF measurement time

Measurement times were selected for both EDXRF instruments by taking into account the coefficient of variation (CV) of five consecutive measurements in a pellet of NIST SRM 1515. Measurement times from 10 to 300 s were evaluated, and the CV varied from 0.4 % for K to 9.5 % for Mn by using 300 s in benchtop EDXRF unit (Fig. 2a), and from 0.1 % for Ca to 3.3 % for P by using 150 s in the handheld system (Fig. 2b). In general, CV lower than 10 % fits for the intended purpose aiming at plant nutrition diagnosis.

Calibration models and analytical figures of merit

Figure 3 shows the benchtop and handheld EDXRF calibration curves for selected elements (K, S and Fe) obtained with pressed pellets of comminuted leaves from 23 varieties of sugar cane.

Correlation coefficients (r) from 0.9601 to 0.9918 and from 0.9094 to 0.9948 were achieved for benchtop and handheld EDXRF instruments, respectively, for all tested analytes (Table 2). For both systems, the results were also equivalent in relation to the detection of possible outliers, as can be observed for the sample with higher K mass fraction (Figures 3a and 3b). This sample (IAC85-5453, with 15.4 g kg^{-1} K) presented comparable relative error of prediction of 12 and 13 % for benchtop and handheld calibration models, respectively.

As the y-intercept of the calibration equation for Fe Kα 6.40 keV in the handheld EDXRF was 200 times higher than that one obtained with the benchtop system, and the ratio of the slopes of the corresponding calibration curves was approximately 20 (Figure 3f), the relationship between the corresponding ratios of y-intercepts and slopes was approximately 10. This is an indication that there was a systematic contribution in the iron X-ray intensity measurements from all test samples in the handheld system. This phenomenon is likely due to the unwanted radiation from the fluorescence of iron impurities in the sample holder components that may generate a characteristic Fe X-ray peak on the spectrum.[61] A cellulose free iron sample was analyzed by both benchtop and handheld units to confirm this assumption. It was found that the data from the handheld spectrometer presented a significant characteristic Fe Kα (6.40 keV) signal, and this was not observed when the benchtop unit was used. Nevertheless, this background contribution can be easily corrected.

The calculated PRESS and RMSEP parameters (Table 2) may provide information on the predictive ability of the calibration models. Higher performance of the mathematic modeling is related to the lower PRESS and RMSEP values. The calibration models derived from the use of benchtop and handheld instruments presented appropriate predictive ability (Table 2).

The LOD values (Table 2) were consistent with data available in the literature for the analysis of vegetal material by EDXRF methods using portable and laboratory units. Reidinger et al.[35] evaluated a portable EDXRF spectrometer for the determination of Si and P in plant material obtaining 140 and 130 mg kg^{-1} as limits of detection, respectively. Furthermore, Pereira et al.[45] used a benchtop EDXRF instrument for the elemental analysis of tea leaves achieving the following limits of detection: 228 mg kg^{-1} K, 184 mg kg^{-1} Ca, 40 mg kg^{-1} Fe and 25 mg kg^{-1} Mn.

By analyzing the RMSEP and limit of detection data, one can indicate both instruments for plant nutrition diagnosis. For instance, for sugar cane crops this assumption fits to this purpose just looking at the critical values of nutrients and beneficial elements investigated herein: 1.9 g kg^{-1} P, 9 g kg^{-1} K, 2 g kg^{-1} Ca, 1.3 g kg^{-1} S, 50 mg kg^{-1} Fe, 16 mg kg^{-1} Mn and 5 g kg^{-1} Si.[4] Although the detection of lighter elements can be limited by their low fluorescent yields[62-63] [e.g. Si (5.0 %), P (6.4 %) and S (8.0 %)[59]], and their measurements could be favored by using low atomic number X-ray tube anodes (e.g. Cr),[62] both EDXRF systems used herein (Rh anodes) enable the simultaneous determination of all tested analytes with appropriate figures of merit, particularly the limits of detection.

Moreover, the reproducibility of both EDXRF methods, estimated by the coefficient of variation from measurements carried out in 3 different pellets from each comminuted laboratory sample, were also appropriate being lower than 13 % for all tested analytes (Table 2).

For sake of information, data from the analysis of the same set of sugar cane leaves by μ-EDXRF described elsewhere[9] were also included in Table 2. The RMSEP values of all methods were comparable, which gives an additional reinforcement on the suitability of calibration models by using matrices with similar chemical and physical composition aiming at plant analysis using different EDXRF methods. When comparing the LOD data one can perceive that benchtop and handheld EDXRF presented best values, especially for the low atomic number elements, such as silicon and phosphorus. The LOD values of μ-EDXRF, although also suitable for plant nutrition diagnosis, are affected by the inherent small spot size (50 μm) and by measurements carried out under air atmosphere.

Under the established experimental conditions, the obtained precision, trueness and limits of detection were appropriate for both EDXRF systems. Notwithstanding, validation should also provide confidence to the analyst to know in advance if the conditions of the selected method are fully appropriate. In this case, we would like to address additional information that may help the analyst for the most suitable option towards benchtop and/or handheld choice:

a) The minimum time to start the handheld measurements takes less than 1 min, while the benchtop unit requires at least 30 min for the first measurement, due to the X-ray tube stabilization.

b) In terms of analytical throughput, the benchtop unit can analyze up to 16 pellets in 2 h, fully automated, including the time required to reach 0.2 torr pressure inside the chamber. It should be mentioned that even for pellets previously stored in a desiccator, the vacuum system takes at least 30 min to reach the target pressure for analysis. When operating the handheld equipment, approximately 15 pellets can be analyzed per hour, even considering the time involved for test sample changing.

c) The measurement times of both systems were optimized to obtain the minimum coefficients of variation, however the analyst may choose higher or lower times depending on the desired compromise between sampling throughput and acceptable precision.

d) The operation of handheld EDXRF equipments must follow safety precautions for the protection of an individual's body against X-ray radiation exposure. The safety devices incorporated in the mobile system used herein follows the recommendation of The Society for Radiological Protection of UK:[64] (i) a clear indication when X-rays is "on", (ii) appropriate stand and metal enclosure when analyzing small objects, and (iii) low-count rate safety sensor which cut-off the X-ray excitation beam when the sample is absent. The steps (ii) and (iii) must be strictly followed to avoid radiation exposure since the dose rates may exceed 1 Sv h^{-1} at the aperture of the handheld EDXRF equipment. In addition, for *in situ* analysis, the analyst must be aware about the best operational practices by carefully reading the safety guidelines from the user's manual.

Conclusions and perspectives

Both benchtop and handheld EDXRF units exhibit similar performances, and they are able to provide useful data for plant nutrition diagnosis relying on simultaneous determinations of P, K, Ca, S, Fe, Mn and Si. The systematic experiments carried out with laboratory samples constituted by leaves of 23 sugar cane varieties, previously analyzed by ICP OES validated procedure, proved to be very useful to build appropriate calibration models. Data produced herein may be useful to check the quality of mass fraction calculations based on EDXRF fundamental parameters. Giving the inherent non-destructive nature of EDXRF, it permits to analyze the same sample pellet with handheld and laboratory units. Consequently, both methods can be used for data cross-validation in analytical quality control.

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LIST OF TABLES

Table 1 - Operational conditions for Benchtop and Handheld EDXRF instruments

Equipment	Spot size (mm)	Spectral region (keV)	Measuring condition	Filter	Tube voltage (kV)	Tube current (µA)	Measuring time (s)	Count rate[*] (kcps)	Dead time (%)
Benchtop	5	1.00 – 40.95	Vacuum (0.2 torr)	No	40	56	300	15	31
Handheld	3	1.00 – 40.95	Vacuum (2 torr)	No	40	12	150	50	14

[*] Total count rate (kilo counts per second - kcps) obtained for the entire spectrum of the sample CTC 17

Table 2 - Analytical figures of merit in benchtop, handheld, and μ-EDXRF[*] analysis

Element	Equipment	LOD[**]	LOQ[**]	r	PRESS	RMSEP	CV range (%)
P	Benchtop	0.10	0.30	0.9674	0.07	0.05	0.6 – 6.5
	Handheld	0.25	0.75	0.9849	0.08	0.06	0.4 – 6.5
	μ-EDXRF	0.50	1.5	0.9501	0.16	0.08	2.0 – 13
K	Benchtop	0.14	0.42	0.9601	9.3	0.63	1.0 – 2.3
	Handheld	0.09	0.27	0.9094	11	0.70	0.03 – 2.2
	μ-EDXRF	0.31	0.93	0.9703	6.5	0.53	0.3 – 3.3
Ca	Benchtop	0.06	0.18	0.9895	0.93	0.20	0.4 – 3.3
	Handheld	0.06	0.18	0.9839	0.58	0.16	0.1 – 2.1
	μ-EDXRF	0.45	1.35	0.9902	0.46	0.14	0.4 – 4.0
S	Benchtop	0.09	0.27	0.9903	0.027	0.03	0.5 – 3.8
	Handheld	0.13	0.39	0.9948	0.035	0.04	0.5 – 3.5
	μ-EDXRF	0.19	0.57	0.9851	0.025	0.03	0.7 – 7.5
Fe	Benchtop	20	60	0.9918	1624	8.4	0.2 – 6.0
	Handheld	20	60	0.9603	2162	9.7	0.2 – 1.8
	μ-EDXRF	60	180	0.9847	3241	12	0.7 – 16
Mn	Benchtop	20	60	0.9908	198	2.9	1.2 – 13
	Handheld	20	60	0.9849	249	3.3	0.9 – 7.7
	μ-EDXRF	30	90	0.9711	551	4.9	1.3 – 14
Si	Benchtop	0.20	0.60	0.9892	3.8	0.41	0.2 – 6.8
	Handheld	0.50	1.5	0.9832	3.0	0.36	0.4 – 3.8
	μ-EDXRF	2.3	6.9	0.9933	6.8	0.54	0.6 – 16

[*] Data from Guerra et al.[9]

[**] LOD = 3.3σ/slope; LOQ = 10σ/slope; P, K, Ca, S and Si: g kg^{-1}; Fe and Mn: mg kg^{-1}

FIGURE CAPTIONS

Figure 1 – EDXRF spectra from a pellet of sugar cane leaves (sample CTC 17) obtained by benchtop and handheld instruments.

Figure 2 – Influence of measurement time for (a) benchtop and (b) handheld EDXRF systems. Data obtained with NIST SRM 1515. Coefficients of variation (CV) based on five replicate measurements in the pellet (test sample).

Figure 3 – Benchtop and handheld EDXRF calibration curves for: (a) and (b) K Kα 3.31 keV, (c) and (d) S Kα 2.31 keV, and (e) and (f) Fe Kα 6.40 keV, obtained with pressed pellets from leaves of 23 varieties of sugar cane. Vertical error bars correspond to ± 1 standard deviation of EDXRF results (n = 3 pellets per sample), and horizontal error bars to ± 1 standard deviation of ICP OES results (n = 3 digests). Dotted lines represent 95 % confidence bands.

Figure 1

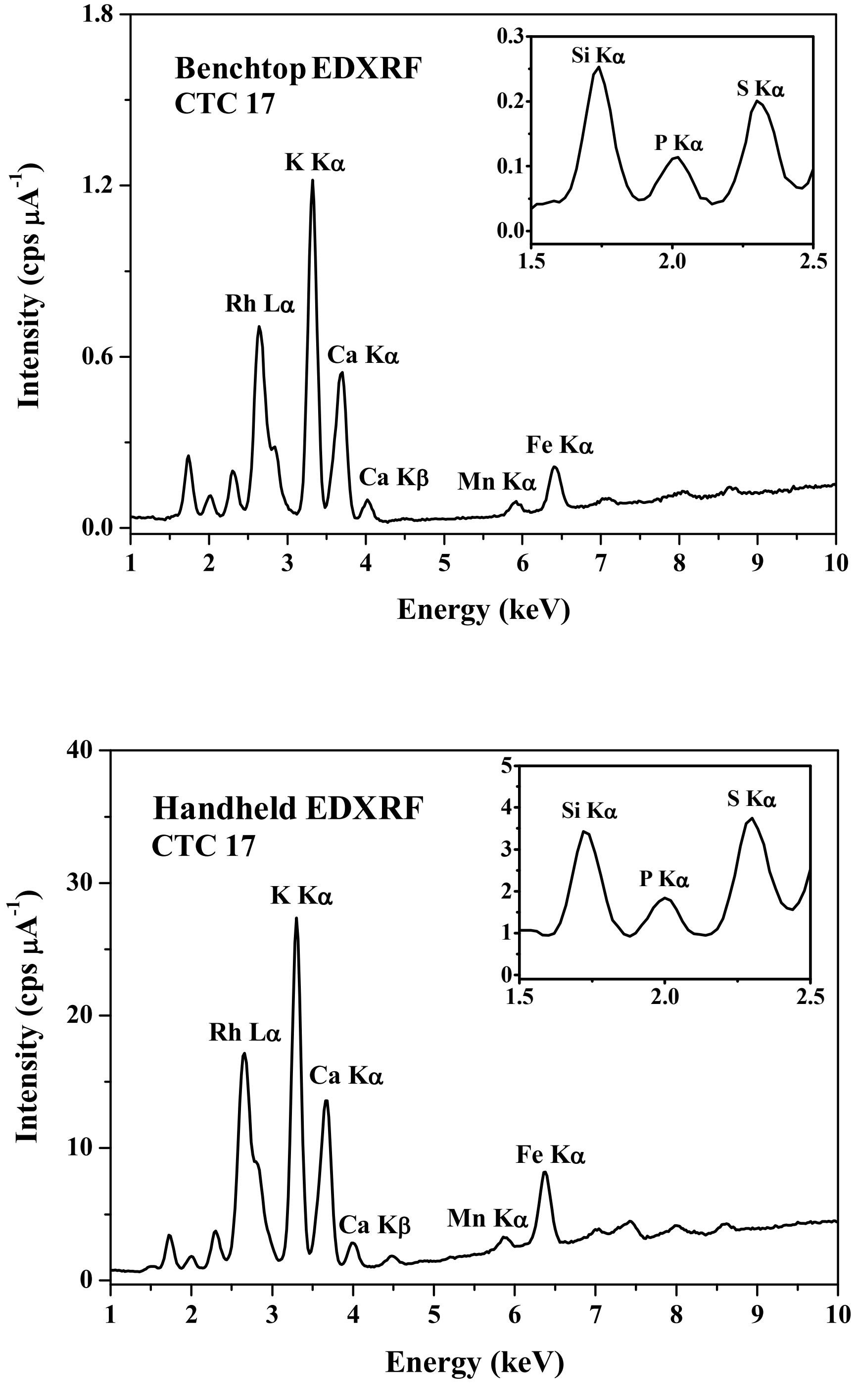

Benchtop EDXRF
CTC 17
Intensity (cps µA^{-1})
Energy (keV)
1.8
1.2
0.6
0.0
1
2
3
4
5
6
7
8
9
10
K Kα
Rh Lα
Ca Kα
Ca Kβ
Mn Kα
Fe Kα
0.3
0.2
0.1
0.0
1.5
2.0
2.5
Si Kα
P Kα
S Kα
Handheld EDXRF
CTC 17
Intensity (cps µA^{-1})
Energy (keV)
40
30
20
10
0
K Kα
Rh Lα
Ca Kα
Ca Kβ
Mn Kα
Fe Kα
5
4
3
2
1
0
Si Kα
P Kα
S Kα

Figure 2

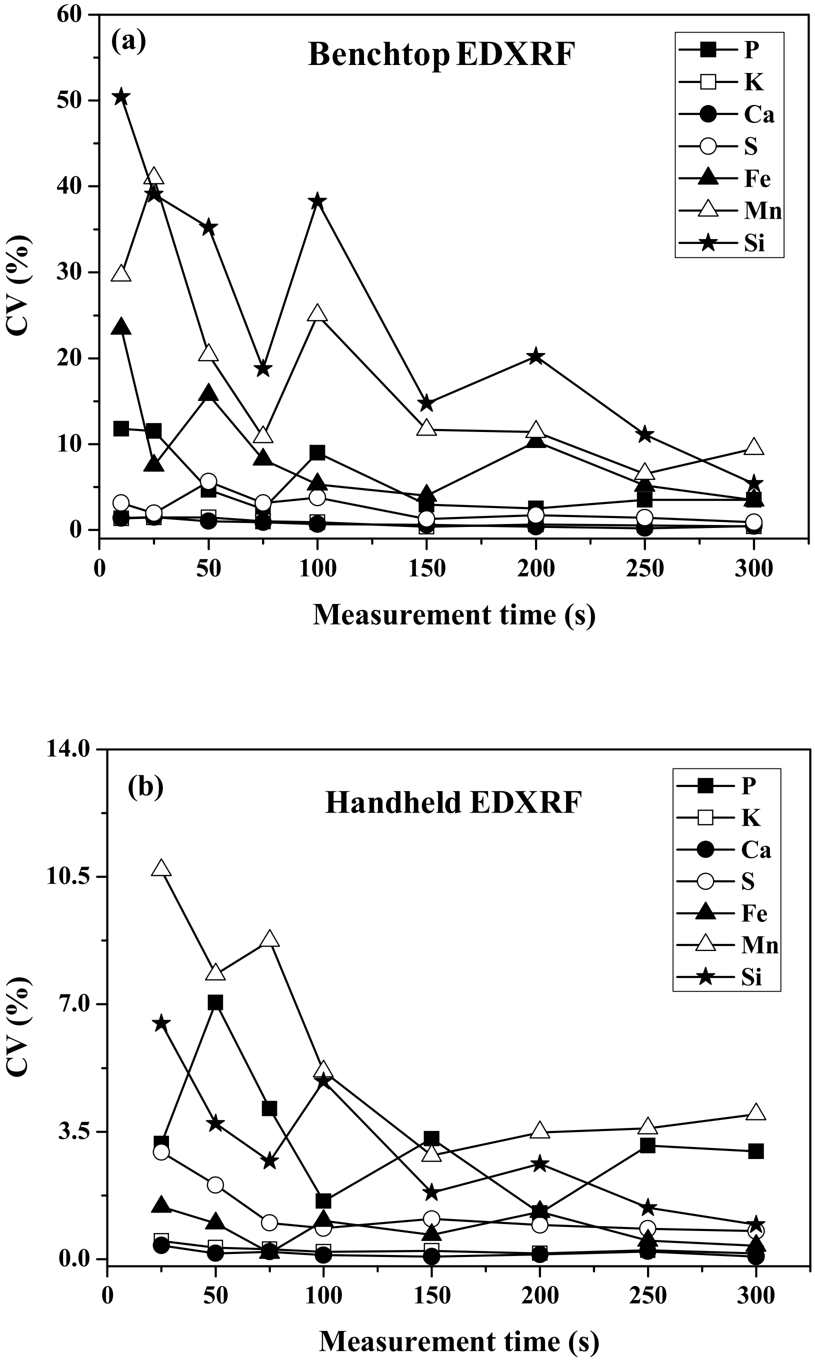
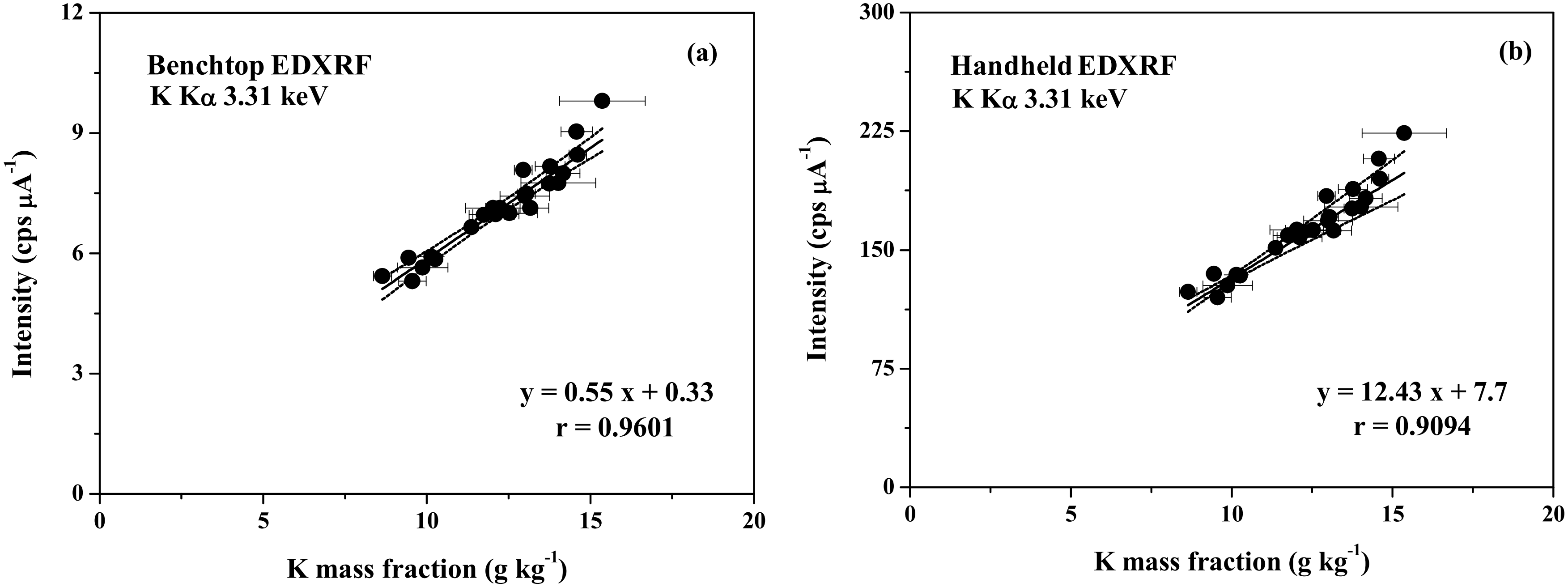
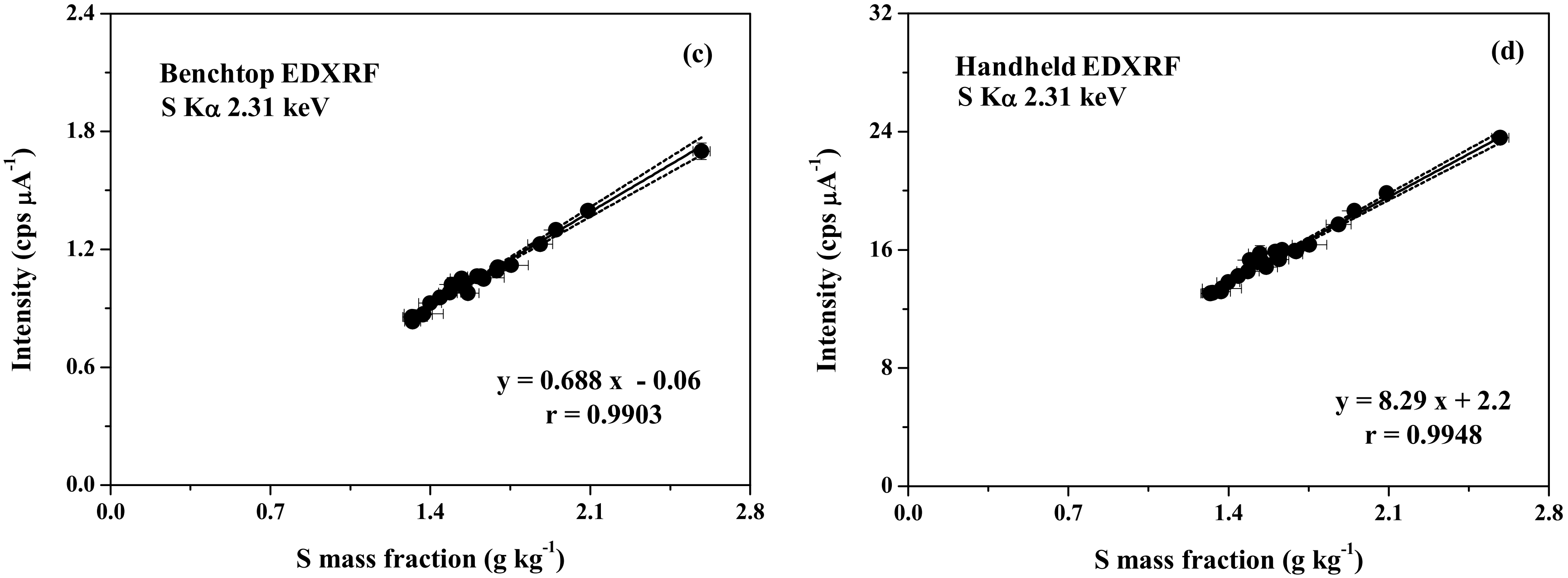

(a)
Benchtop EDXRF
CV (%)
Measurement time (s)
60
50
40
30
20
10
0
0
50
100
150
200
250
300
P
K
Ca
S
Fe
Mn
Si
(b)
Handheld EDXRF
CV (%)
Measurement time (s)
14.0
10.5
7.0
3.5
0.0
0
50
100
150
200
250
300
P
K
Ca
S
Fe
Mn
Si

Figure 3


Benchtop EDXRF
K Kα 3.31 keV
(a)
y = 0.55 x + 0.33
r = 0.9601
Intensity (cps μA-1)
K mass fraction (g kg-1)
0
3
6
9
12
0
5
10
15
20
Handheld EDXRF
K Kα 3.31 keV
(b)
y = 12.43 x + 7.7
r = 0.9094
Intensity (cps μA-1)
K mass fraction (g kg-1)
0
75
150
225
300
0
5
10
15
20

Continuation… Figure 3



Continuation… Figure 3