Quantitative determination of metals in radish using x-ray fluorescence spectrometry†

M. J. Anjos,1,2* R. T. Lopes,1 E. F. O. Jesus,1 S. M. Simabuco3 and R. Cesareo4

1 Universidade Federal do Rio de Janeiro/COPPE, Laboratório de Instrumentação Nuclear
2 Universidade do Estado do Rio de Janeiro, Instituto de Física, Rio de Janeiro, RJ, Brazil
3 Universidade Estadual de Campinas, FEC, Campinas, SP, Brazil
4 Università di Sassari, Istituto di Matematica e Fisica, Sassari, Italy

Received 7 March 2001; Accepted 15 October 2001

Using energy-dispersive X-ray fluorescence analysis with a Ti-filtered x-ray tube it was possible to determine the concentrations of several elements, such as K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr, Zr and Pb, at ppm levels in radish plants (root and foliage) cultivated in soils treated with concentrations of 10, 20 and 30 t ha−1 of organic compost from urban garbage. A significant increase was observed in the concentrations of K, Ca, Mn, Fe, Zn, Rb and Pb in radish plants cultivated in the treated soils in comparison with a control soil. The results suggest that radish plants can be used as bioindicator of contamination of agricultural soils. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

The contamination of agricultural soils with metals is one of the most severe ecological problems in the contemporary world. The metals can be transferred to plants which are cultivated in those soils and consequently can enter direct or indirectly the human alimentary chain.1,2 Approximately 92 elements are found naturally in soils, of which less than 20 are essential for the growth and nutrition of the plants and are classified according to their needs: the primary elements are those which the plants need in large quantities such as calcium, phosphorus, iron and sulfur. It is cultivated practically worldwide and, in spite of being a culture of small importance in terms of planted area, it is important in large numbers of small properties in green belts. An interesting characteristic of radish culture is that it can be used as a cash culture among others, with a longer cycle and with predefined times of planting. It is interesting because, in addition to being relatively rustic, it has a very short cycle of cultivation time between 20 and 30 days. This characteristic is very important for environmental analysis because it suggests that the radish, compared with other cultures, could be used as a bioindicator of environmental pollution of agricultural soils.6–9

The objective of this work was to show the viability of the use of energy-dispersive x-ray fluorescence spectrometry for the determination of metal concentrations in radish plants. This information can help to detect metal contamination in agricultural soils and to indicate the use of radish plants as a bioindicator of contamination in agricultural soils.

THEORETICAL BACKGROUND

X-ray fluorescence (XRF) spectroscopy is one of the primary applications in x-ray science and it has been used as an analytical tool for a very long time, almost since the time of its discovery 100 years ago. XRF is used normally to determine the concentrations of different elements in a sample with advantages of good sensitivity, non-destructiveness and a simple relation to the fundamental physics of atom–radiation interaction. This relation is normally expressed in terms of a so-called ‘fundamental parameter’ model used for quantifying the XRF results.10,11

For excitation with monoenergetic photons, the relationship between the fluorescence intensity of a characteristic Kα
or La line and the concentration of an element present in the sample, is given by

\[
l_i = S_i W_i (\rho M D) \frac{1 - \exp(-\chi_i \rho M D)}{\chi_i \rho M D}
\]

where \( S_i \) = x-ray sensitivity of the spectrometer for element \( i \), \( W_i = \text{weight fraction of element } i \), \( \rho M D \) = superficial density of the matrix (g cm\(^{-2}\)) and \( \chi_i \) = total mass absorption coefficient, defined by

\[
\chi_i = \frac{\mu M(E_i)}{\sin(\psi_1)} + \frac{\mu M(E_i)}{\sin(\psi_2)}
\]

where \( \psi_1 \) = radiation incident angle (between the incident beam direction and sample surface), \( \psi_2 \) = radiation emergent angle (between the sample surface and emergent beam direction), \( \mu M(E_i) \) = mass absorption coefficient of the matrix for the excitation energy \( E_i \) and \( \mu M(E_i) \) = mass absorption coefficient of the matrix for the XRF energy \( E_i \).

**RESULTS AND DISCUSSION**

Table 1 presents the results for average elemental concentrations calculated with three replicates and their deviations in comparison with SL-1 certified values. The results based on triplicate measurements had an error of the order of 10%, close to the errors cited in the literature. Figure 2 shows the concentrations of K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Sr, Zr and Pb in the radish plants (root and foliage) cultivated in the control soil. K and Pb showed higher concentrations in the root of the radish plants. On the other hand, Ca, Ti, Mn, Fe, Cu, Zn, Br, Sr and Zr showed higher concentrations in the leaves. Zirconium was not detected in the root samples.

**EXPERIMENTAL**

The experimental setup shown in Fig. 1 is composed of an x-ray tube (Oxford, 30 kV, 50 μA and W anode), an ORTEC Si(Li) detector, with an energy resolution of about 180 eV at 5.9 keV, and an ORTEC multichannel analyser. The angle between the incident beam and sample surface is 16° and that between the sample surface and emergent beam is 90°. The x-ray beam is made quasi-monochromatic by using a Ti filter. We have produced filters for a large number of elements and with various surface densities (mg cm\(^{-2}\)) by mixing powder of an element or of compounds with boric acid. This mixture is prepared in pellet form.

The elemental sensitivity is usually determined by the measurement of the characteristics of the x-rays emitted by standards, containing only one element. The utilization of standards prepared in the laboratory with commercially available pure elements or compounds has been shown to be efficient for the determination of the elemental sensitivity in XRF systems because they are inexpensive and can be easily prepared. To correct for the absorption effects, \(^{12-14}\) two multielemental thick targets containing Ti, Mn, Ni, Zn, Ge, Br, Sr and Nb (target 1) and Cr, Fe and Cu (target 2), and a radioactive source of Am-241 were used.

Samples of radish plants were collected at the Experimental Station of the Company of Agricultural Research of the State of Rio de Janeiro in Brazil (PESAGRO-RJ). The sampling was performed in four blocks: block A (control soil), block B (soil treated with a dose of 10 t ha\(^{-1}\) of organic compost), block C (soil treated with a dose of 20 t ha\(^{-1}\) of organic compost) and block D (soil treated with a dose of 30 t ha\(^{-1}\) of organic compost). The samples were dried at 80°C for ~12 h, powdered (325 mesh) and diluted with boric acid in a 1:4 ratio (100 mg of sample and 400 mg of H\(_3\)BO\(_3\)). They were then submitted to a pressure of 203 MPa for 10 min, obtaining 2.5 cm diameter pellets of 100 mg cm\(^{-2}\) surface density. Three replicates were made for each sample. To evaluate the accuracy of the system, SL-1/AIEA certified samples were also prepared in pellet form as described before and measured.

**Table 1. Elemental concentrations determined by EDXRF and certified in SL-1/AIEA**

<table>
<thead>
<tr>
<th>Element</th>
<th>EDXRF</th>
<th>SL-1/AIEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.40%</td>
<td>1.50%</td>
</tr>
<tr>
<td>Ca</td>
<td>0.27%</td>
<td>0.25%</td>
</tr>
<tr>
<td>Ti</td>
<td>0.54%</td>
<td>0.52%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.36%</td>
<td>0.35%</td>
</tr>
<tr>
<td>Fe</td>
<td>6.90%</td>
<td>6.75%</td>
</tr>
<tr>
<td>Ni</td>
<td>40 ppm</td>
<td>44 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>32 ppm</td>
<td>30 ppm</td>
</tr>
<tr>
<td>Zn</td>
<td>214 ppm</td>
<td>223 ppm</td>
</tr>
<tr>
<td>Rb</td>
<td>123 ppm</td>
<td>113 ppm</td>
</tr>
<tr>
<td>Sr</td>
<td>85 ppm</td>
<td>80 ppm</td>
</tr>
<tr>
<td>Zr</td>
<td>201 ppm</td>
<td>241 ppm</td>
</tr>
</tbody>
</table>

**Figure 1.** Schematic diagram of the experimental setup.

**Figure 2.** Metal concentrations in radish plants (roots and foliage) cultivated in the control soil.
Figures 3 and 4 show the concentrations of the elements found in the samples of radish roots. The concentrations of K, Ca, Mn, Fe, Cu, Zn, Rb and Sr increased with increasing dose of organic compost. K, Ca, Fe, Zn and Rb showed concentrations double those found in the control soil, but the concentration of Ti did not change in relation to the same soil. The concentrations of Br and Pb showed a different behavior: they decreased in relation to the control soil to approximately half the value.

Figures 5 and 6 show the concentrations found in the samples of foliage of radish plants cultivated in soils treated with organic compost from urban garbage. Compared with the concentrations in the control soil, the concentrations of K, Ca, Ti, Mn, Fe, Cu, Zn, Rb and Pb measured in the samples were higher than the upper level of the confidence limits (α = 0.05). The concentrations of Sr and Zr were higher than those found in the control soil only for doses of 30 t ha$^{-1}$ of organic compost. The bars shown in Figs 2–6 are the confidence limits to α = 0.05. Table 2 shows the linear correlation between the different doses of organic compost applied in the agricultural soil and the elemental concentration in the radish plants (roots and foliage). K, Ca, Fe, Mn, Cu, Zn and Rb (root samples) and K, Ca, Ti, Fe, Mn, Cu, Zn and Pb (foliage samples) showed strong positive linear correlations. On the other hand, Br, Sr and Pb (root samples) and Sr and Zr (foliage samples) showed weak linear correlations, Br and Pb with negative correlations.

Table 2. Linear correlation between the different doses of organic compost applied in agricultural soil and the elemental concentration in radish plants (roots and foliage)

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
<th>Br</th>
<th>Rb</th>
<th>Sr</th>
<th>Zr</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root</td>
<td>0.90</td>
<td>0.87</td>
<td>0.72</td>
<td>0.82</td>
<td>0.96</td>
<td>0.85</td>
<td>0.90</td>
<td>–0.57</td>
<td>0.89</td>
<td>0.55</td>
<td>–</td>
<td>–0.69</td>
</tr>
<tr>
<td>Foliage</td>
<td>0.86</td>
<td>0.97</td>
<td>0.84</td>
<td>0.97</td>
<td>0.99</td>
<td>0.92</td>
<td>0.93</td>
<td>–0.98</td>
<td>0.96</td>
<td>0.38</td>
<td>0.45</td>
<td>0.83</td>
</tr>
</tbody>
</table>

CONCLUSIONS

This experiment was a preliminary attempt to determine quantitatively metal contamination in radish plants. The results indicate that the values found for K, Ca, Mn, Fe, Zn, Rb and Pb are significantly above the upper confidence limits for the control soil (α = 0.05). There is a positive linear correlation between the different compost doses applied in the soil and the concentrations in the radish plants for some elements: K, Ca, Fe, Mn, Cu, Zn and Rb (root samples) and...
K, Ca, Ti, Fe, Mn, Cu, Zn and Pb (foliage samples). The radish plants were shown to be sensitive to the variations in elemental concentrations in the soil. The results suggest that radish plants can be used as a bioindicator of contamination of agricultural soils. New studies on radish plants and other vegetables with very short cultivation cycles should be carried on in order to define the best vegetable that can be used as a bioindicator of contamination of agricultural soils.

Acknowledgements
The authors thank the Brazilian agencies CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) (bilateral project CNPq–CNR) and FAPERJ (Fundaçao de Amparo a Pesquisa do Estado do Rio de Janeiro) for financial support.

REFERENCES