Short communication

Approximate total Fe content determined by Mössbauer spectrometry: Application to determine the correlation between gamma-ray-emitter activities and total content of Fe phases in soils of the Province of Buenos Aires, Argentina

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A B S T R A C T

Pearson correlation coefficients between ^{40}K, ^{226}Ra and ^{232}Th activities and the total Fe phase fractions yielded by Mössbauer spectroscopy have been calculated for soils of the Province of Buenos Aires, Argentina. Total fractions of Fe phases have been obtained from the relative fractions reported in previous works weighted by the Fe soil content and the recoilless-fraction of each Fe phase. An approximate method based on the relationship between the Mössbauer spectral absorption area (obtained from the ^{57}Fe Mössbauer data) and the total Fe concentration (determined by colorimetric methods, after microwave assisted acid digestion of soil samples) has been used for the first time to determine the Fe concentration in soils with an accuracy of 15%. Protocol to extend the method for unknown samples is also discussed. The determined new coefficients differ from those reported previously. A significant and positive correlation between the total fraction of Fe^{2+} and the ^{40}K activity values has been obtained. This result validates the hypothesis put forward in a previous work, i.e., that illite captures the ^{40}K existing in the soil. In addition, with the new approximation, the Pearson correlation coefficients for the other natural radionuclides give values that indicate that the methodology reported here is appropriate to study the correlations between the activity values with the total fractions of Fe phases.

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1. Introduction

Over clay minerals formation, natural radionuclides incorporate as trace elements in the mineral structures. When both minerals and radionuclides disperse homogeneously and are similarly affected by the formation process, a correlation between major minerals and radionuclide abundances can be expected.

Suresh et al. (2011). For example, this relationship has been analyzed by Montes et al. (2012) for unperturbed soils of La Plata region, Argentina. In the previous study, the authors determined the Pearson correlation coefficients between the activities of ^{40}K, ^{226}Ra and ^{232}Th and the relative fractions of Fe phases (revealed by Mössbauer spectroscopy), since they are related to the existing clay minerals and Fe oxides in that matrix (Murad, 2010; Vandenberghe

and De Grave, 2013). Indeed, when considering results yielded by different techniques (Montes et al., 2012, 2013), the authors concluded that the paramagnetic Mössbauer signals of Fe^{3+} arise from Fe located inside the structure of illite, smectite and kaolinite while Fe^{2+} signal can be attributed only to kaolinite and illite (Vandenberghe and De Grave, 2013). Moreover, Montes et al. (2013), reported that kaolinite is much less abundant than illite, therefore it can be assumed that the principal contribution to the Fe^{2+} phase arise from illite. Thus a correlation between Fe^{2+} and ^{40}K activity values could be presumed, due to the high irreversible retention capacity of potassium by illite. However, the Pearson correlation coefficient determined by Montes et al. (2012) between the Mössbauer Fe^{2+} relative fraction and the ^{40}K activity was not significant.

In the present work, the Pearson correlation coefficients between the total fractions of the Fe phases (relative fractions weighted by Fe concentration and the recoilless-fraction of each Fe

phase) and the ^{40}K, ^{226}Ra and ^{232}Th activities have been evaluated. A novel approximate methodology to assess the total Fe content in soils using the relative areas of the ^{57}Fe Mössbauer resonant spectrum with respect to the non-resonant, jointly with colorimetric methods, was developed.

2. Material and methods

Details on characterization of soil samples, collected in La Plata city region, can be found in previous works (Montes et al., 2012, 2013; 2016; Montes, 2013).

Activity values of ^{40}K, ^{226}Ra and ^{232}Th are given in Montes et al. (2012, 2016). The gamma spectra of soils samples were recorded using a GMX10 gamma EG&G Ortec detector with relative efficiency of 40% and a resolution of 1.97 keV at 1332 keV. The detector was kept inside an EG&G Ortec low-background chamber and was coupled to a standard electronics chain, with a multichannel analyzer of 8192 channels. The energy calibration curve was obtained using specific radioactive sources. The efficiency calibration was performed following the procedure describe by Perillo et al. (1997). Fe phase relative fractions were determined using ^{57}Fe Mössbauer spectroscopy (Montes et al., 2012).

Fe concentration in soils is normally determined with high precision by atomic absorption spectroscopy or photometric methods. However, in both cases the entire procedure can be tedious, expensive and time consuming, requiring sample digestion (EPA, 1996; Van Reeuwijk, 2002). ^{57}Fe Mössbauer spectroscopy, based on the recoil-free resonant absorption of gamma rays in solids, allows determining the Fe phases and its relative fractions (Greenwood and Gibb, 1971). The information from this technique could be used as an alternative method to determine soil Fe concentration, although with lower precision. The advantage of using this technique over conventional ones is that it is nondestructive and, in favorable cases (Fe phase concentration higher than 4%) allows assessing the Fe phases present in the samples.

The parameter used to estimate the Fe concentration is the Mössbauer spectral absorption area (*IAA*), calculated from the spectrum according to:

$$IAA = \left| \frac{\sum_{i=1}^{C} C_i - C_o}{C_o} \right| C_f \left(\frac{RF_{Fe^{3+}(I)} + RF_{Fe^{3+}(I)} + RF_{PRM}}{0.83} + \frac{RF_{Fe^{2+}}}{0.71} \right.$$
$$\left. + \frac{RF_{\alpha - Fe_2O_3}}{0.844} + \frac{RF_{Fe_3O_4}}{0.889} \right) \tag{1}$$

where C_i represents the number of counts in channel i, C_o is the number of counts corresponding to the background of the spectrum and C_f the calibration factor, in (mm/s)/channel, obtained from the spectrometer calibration. RF_i refers to the relative fraction of the i-th Fe phase and the number in the denominators represent the Mössbauer fraction, f, of each fraction (Vandenberghe and De Grave, 2013).

If the Fe concentration is low enough, it is expected that *IAA* display a linear dependence on the Fe content in the absorber (Greenwood and Gibb, 1971; Williams and Brooks, 1975). Therefore, by obtaining a linear relationship between *IAA* and the Fe concentration it is possible to estimate the total Fe concentration in soils by calculating *IAA* from the Mössbauer spectrum.

To determine the *IAA* and Fe concentration relationship, 15 soil samples of Buenos Aires Province and one of Misiones Province (iron rich soils) were digested following the method 3052 of EPA

(1996). Afterwards, the Fe concentration (*Fe$_C$*) of the solution was determined by the classic reaction between the Fe(III) and the thiocyanate ions to yield a red-brown complex ion. The experiments were performed using a Shimadzu UV-mini 1240 spectrophotometer, according to the method proposed by Adams (1995). The Fe concentration in soils was expressed as g Fe/kg of soil, considering the mass of the digested soil. *IAA* was calculated from the Mössbauer spectra as indicated in Equation (1). As explained in previous works, the Mössbauer spectra were taken using 300 mg of soil samples placed in a sample holder of 19 mm diameter, which is the optimum thickness (approximately 105 mg/cm^2) to attain the best signal-to-noise ratio, according to Long et al. (1983).

3. Results and discussion

3.1. IAA and Fe concentration relationship

Table 1 displays the obtained Fe concentrations and the *IAA* values for the 15 analyzed samples. In Fig. 1 *IAA* values as function of Fe concentration are depicted. As it can be seen, *IAA* values obtained for Buenos Aires Province soils (black circles in Fig. 1) display a linear dependence with *Fe$_C$*. However, *IAA* value of Misiones soil (black square in Fig. 1) lies far away from a linear behavior probably because of Fe concentration is not low enough. In order to determine the Fe concentration upper limit were *IAA* vs *Fe$_C$* depicted a linear behavior, the Mössbauer spectra of the Misiones soil were recorded using different absorber thicknesses: diluted samples of 100, 150, 180, 200, 240 and 270 mg per sample. The corresponding *IAA* values are included in Fig. 1 as open squares. For the lower masses, the *IAA* values lie within the linear behavior, but when more massive absorbers are used (240 and 270 mg), *IAA* departs from the linearity and therefore are not considered to the fit.

The linear relationship, considering the data mentioned before, resulted:

$$IAA \left(mm \cdot s^{-1} / channel \right) = a + b * Fe_C \tag{2}$$

with $a = 0.02 \pm 0.01$ mm s^{-1}/channel, and $b = 0.0020 \pm 0.0003$ (mm s^{-1}/channel)/(g/kg) with a R-squared of 0.83.

Equation (2), enables to determine the total content of Fe in soils within a concentration range from 25 to ≈ 110 g/kg. For soil samples with Fe concentration higher than 110 g Fe/kg and *IAA* values less than 0.23 mm s^{-1}/channel, a thinner absorber with a less massive sample must be used. Using this methodology, Fe concentration can be estimated with a perceptual error around 15%.

This method proposes a way to estimate, roughly but simply and reliably, the total amount of iron in unprocessed soil samples. To use it properly, Fe concentration must be low enough. To guarantee this, at least, two independent measurements must be performed: one using 300 mg of sample and the other diluting the sample 1:2 or 1:3. If the samples have an adequate Fe concentration the IAA values will lie in the linear region (being the results for the IAA value of the diluted sample 1/2 or 1/3 from the one obtained for 300 mg). Contrary, if the Fe concentration is not low enough, the IAA value for 300 mg must be discarded and the diluted sample must be considered.

3.2. Correlation between total Fe phases and ^{232}Th, ^{226}Ra and ^{40}K activities

The determined Fe phases for La Plata soils using Mössbauer spectroscopy were previously reported and can be resumed as: Fe^{3+}(I), Fe^{3+}(II), Fe^{2+}, hematite (hem), magnetite and a compound

Table 1
Fe concentration Fe_C and *IAA* values for the studied samples. B denotes Buenos Aires province soils and M Misiones soil.

Soil sample	Fe_C (g/kg)	*IAA* (mm s^{-1}/channel)	Soil sample	Fe_C (g/kg)	*IAA* (mm s^{-1}/channel)
B1	26.5 ± 0.8	0.08 ± 0.01	B9	62.0 ± 2.0	0.15 ± 0.02
B2	34.8 ± 0.9	0.12 ± 0.03	B10	31.9 ± 0.9	0.10 ± 0.01
B3	51.0 ± 1.0	0.13 ± 0.03	B11	58.0 ± 1.0	0.16 ± 0.02
B4	27.4 ± 0.8	0.06 ± 0.02	B12	56.0 ± 1.0	0.17 ± 0.02
B5	34.6 ± 0.9	0.07 ± 0.02	B13	36.0 ± 0.9	0.08 ± 0.02
B6	32.6 ± 0.9	0.06 ± 0.03	B14	43.0 ± 1.0	0.09 ± 0.03
B7	34.7 ± 0.9	0.05 ± 0.02	M1	168 ± 2.0	0.23 ± 0.03
B8	59.0 ± 2.0	0.13 ± 0.02			
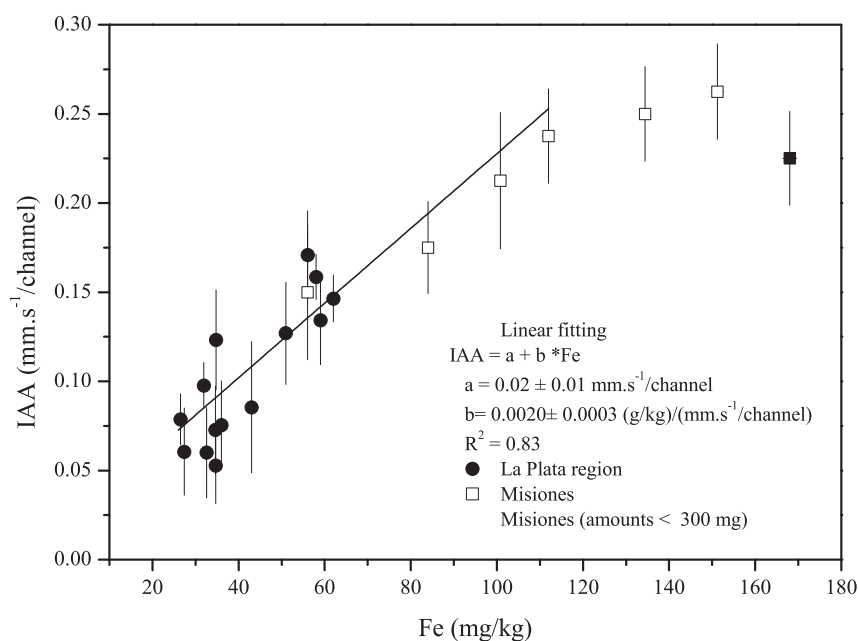
Fig. 1. Relationship between *IAA* and the Fe concentration Fe_C. Circles represent the data from soils of Buenos Aires province; full squares display Misiones province soil while the hollow squares symbolize the diluted Misiones samples. The continuous line is the result of the linear fit whereas the dash line represents the extrapolation of the linear fit.

undergoing paramagnetic relaxation at RT (Montes et al., 2012, 2013).

The total Fe content of each Fe phase was obtained considering the relative fraction, the recoilless-fraction of each Fe phase and the Fe concentration, obtained by the methodology described in Section 2.

The total fractions of each Fe phase are reported in Table 2. Data of magnetite is disregarded because the concentration of this phase cannot be determined for most of the samples. Paramagnetic relaxation data could not be associated to a particular mineral, so the results are not considered.

The Pearson correlation coefficients between the total fractions of the Fe phases and the activity values were calculated (0.01 confidence level). Table 3 displays the obtained coefficients including those reported previously (i.e. relative fractions/radionuclides) as subscripts (Montes et al., 2012).

A significant and negative correlation between the total fraction of hematite and the activity values of ^{226}Ra and ^{40}K was determined, although the correlation coefficients results relatively low and the data of activity vs hematite content (not shown here) do not present a marked trend.

The correlations between ^{226}Ra, ^{232}Th and ^{40}K activity values with the total fractions of the Fe^{3+}and Fe^{2+}phases are significant and positive. Regarding the ^{232}Th and the Fe phases correlations

these seem to be weaker than the others, probably due to the fact that ^{232}Th can form insoluble complexes (Coppens, 1979) and therefore unlikely to be incorporated into the mineral structures.

Regarding ^{226}Ra, it must be pointed that when the relative fractions were considered none correlation was observed as it was reported by Montes et al. (2012), contrary to the result reached in this work. The latter intriguing observation is supported by the fact that among the alkali Ra is the one most strongly sorbed by ion exchange on clay minerals (IAEA, 2014).

The most meaningful result obtained from the new Pearson coefficients is the significant and positive correlation obtained between the total fractions of Fe^{2+} phase and the ^{40}K activity values (see also Fig. 2). As mentioned above, the Fe^{2+} phase arise from the presence of kaolinite and illite. Nevertheless, it should be remarked that in these soils kaolinite is much less abundant than illite (Montes et al., 2013; Montes, 2013). Hence, it is expected that the contribution to the Fe^{2+} phase attributed to illite should be dominant compared with the kaolinite one.

Mössbauer spectra of two soil samples, each one from the two geomorphological units of the region, were taken after heating the soils to a temperature of 573 K. As suggested by Murad (2010), that treatment yields the vanishing of the Fe^{2+} phase of illite. The Mössbauer results indicate a strong decrease of the Fe^{2+} signal, corroborating that the Fe^{2+} phase is mainly originated in illite.
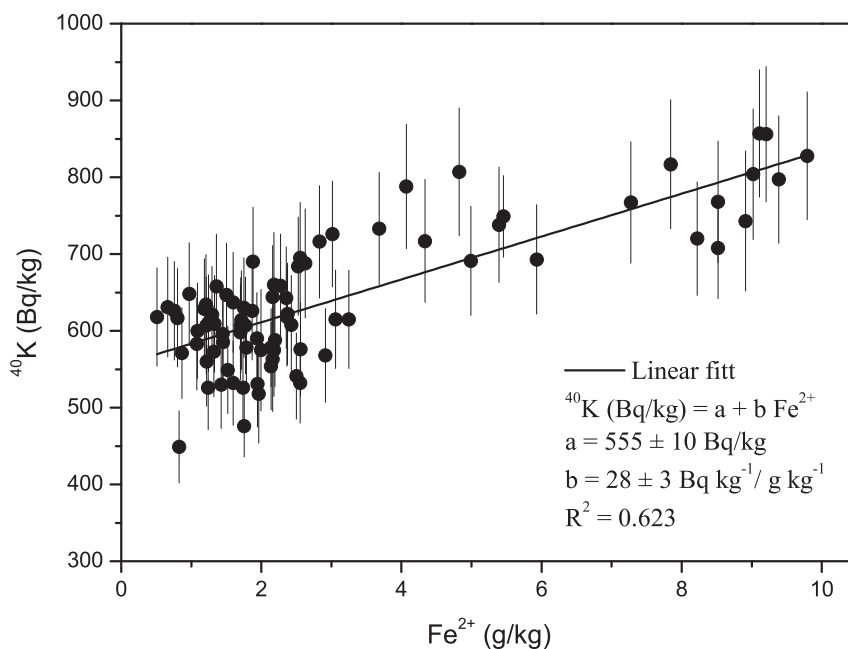
Table 2

Fe concentration in the soils (in g/kg) and the total concentration of Fe phases (in g/kg) obtained weighting the Fe phase relative fractions with Fe concentration in soil. SP1, SP2, SP3 and SP4 are the Soil code (SC) described in Montes et al. (2012, 2013), while LH and RP are the SC used in Montes et al. (2013). The SC described by number/number is the nomenclature used in Montes et al. (2016).

SC/depth	Fe	$Fe^{3+}(I)$	$Fe^{3+}(II)$	Fe^{2+}	Hem
SP1/2.3	27 ± 3	8 ± 1	5 ± 1	1.9 ± 0.3	3.9 ± 0.3
SP1/4.4	31 ± 3	9 ± 2	6 ± 2	2.6 ± 0.8	4.0 ± 1.0
SP1/9.4	35 ± 4	11 ± 2	7 ± 1	2.9 ± 0.5	4.8 ± 0.9
SP1/18.3	36 ± 4	10 ± 1	6 ± 1	2.6 ± 0.5	4.9 ± 0.9
SP1/25.5	36 ± 4	11 ± 1	6 ± 1	2.6 ± 0.5	4.9 ± 0.6
SP1/27.5	49 ± 4	20 ± 2	10 ± 2	2.9 ± 0.6	4.3 ± 0.6
SP1/29.3	62 ± 4	26 ± 3	14 ± 2	3.7 ± 0.8	4.9 ± 0.7
SP1/37.3	63 ± 4	27 ± 3	12 ± 2	3.7 ± 0.8	5.5 ± 0.7
SP1/45.6	62 ± 4	28 ± 2	14 ± 2	2.9 ± 0.8	4.8 ± 0.7
SP1/49.0	64 ± 4	29 ± 2	13 ± 2	3.0 ± 0.8	5.6 ± 0.7
SP2/1.8	20 ± 3	9 ± 2	6 ± 1	2.4 ± 0.6	4.5 ± 0.9
SP2/7.3	25 ± 3	11 ± 2	7 ± 1	3.1 ± 0.4	7.0 ± 1.0
SP2/12.0	25 ± 3	13 ± 2	6 ± 1	2.6 ± 0.6	6.0 ± 1.0
SP2/21.8	25 ± 3	13 ± 2	6 ± 1	2.6 ± 0.6	5.3 ± 0.9
SP2/29.0	47 ± 4	32 ± 3	10 ± 2	4.1 ± 0.9	7.0 ± 1.0
SP2/35.5	47 ± 4	32 ± 3	10 ± 2	4.1 ± 0.9	7.5 ± 0.9
SP2/41.5	47 ± 4	30 ± 2	11 ± 2	4.1 ± 0.9	7.4 ± 0.9
LH/3.5	20 ± 3	8 ± 2	8 ± 3	1.8 ± 0.8	5 ± 1
LH/11.5	20 ± 3	10 ± 2	7 ± 2	2.1 ± 0.8	5 ± 1
LH/17.5	20 ± 3	9 ± 2	7 ± 2	1.8 ± 0.8	5 ± 1
LH/21.5	20 ± 4	9 ± 2	6 ± 2	2.4 ± 0.8	7 ± 1
LH/27.3	27 ± 4	15 ± 2	7 ± 2	2.4 ± 0.6	6 ± 1
LH/36.3	34 ± 4	18 ± 3	10 ± 2	2.9 ± 0.7	6 ± 1
LH/42.1	40 ± 4	27 ± 3	12 ± 2	2.8 ± 0.8	6 ± 1
LH/48.8	40 ± 4	24 ± 3	14 ± 2	2.8 ± 0.8	6 ± 1
SP3/4.0	59 ± 4	47 ± 3	18 ± 2	8.0 ± 1.0	2.6 ± 0.9
SP3/10.5	64 ± 4	53 ± 3	21 ± 2	8.0 ± 1.0	1.9 ± 0.9
SP3/17.8	70 ± 4	58 ± 3	22 ± 1	7.0 ± 1.0	2.0 ± 1.0
SP3/22.8	70 ± 4	59 ± 3	21 ± 2	9.0 ± 1.0	2.0 ± 1.0
SP3/29.8	70 ± 4	57 ± 3	21 ± 2	9.0 ± 1.0	2.0 ± 1.0
SP3/34.3	64 ± 4	53 ± 3	20 ± 2	8.0 ± 1.0	1.8 ± 0.9
SP3/39.3	64 ± 4	53 ± 3	20 ± 2	8.0 ± 1.0	1.9 ± 0.9
SP3/48.5	70 ± 4	58 ± 3	23 ± 2	9.0 ± 1.0	3.0 ± 1.0

SC/depth	Fe	$Fe^{3+}(I)$	$Fe^{3+}(II)$	Fe^{2+}	Hem
SP4/3.0	37 ± 4	24 ± 2	12 ± 2	4.5 ± 0.8	2.1 ± 0.6
SP4/6.5	31 ± 3	20 ± 2	10 ± 1	4.3 ± 0.8	0.5 ± 0.4
SP4/12.5	59 ± 4	45 ± 3	18 ± 2	9.0 ± 1.0	0.9 ± 0.8
SP4/18.5	64 ± 4	49 ± 3	19 ± 2	9.0 ± 1.0	0.9 ± 0.9
SP4/23.3	75 ± 4	61 ± 3	22 ± 2	9.0 ± 1.0	2.0 ± 1.0
SP4/28.3	75 ± 4	58 ± 3	23 ± 2	9.0 ± 1.0	2.0 ± 1.0
SP4/33.5	65 ± 4	42 ± 3	18 ± 2	9.0 ± 1.0	1.9 ± 0.9
SP4/40.0	65 ± 4	50 ± 3	17 ± 2	10 ± 1.0	0.9 ± 0.9
SP4/44.8	70 ± 4	51 ± 3	19 ± 2	10 ± 1.0	3.0 ± 1.0
RP/3.5	14 ± 4	7 ± 2	4 ± 1	2.2 ± 0.8	2.2 ± 0.8
RP/11.0	26 ± 4	13 ± 2	7 ± 1	5.0 ± 1.0	2.6 ± 0.8
RP/17.5	26 ± 4	13 ± 2	6 ± 1	6.0 ± 1.0	3.0 ± 0.9
RP/22.0	26 ± 4	13 ± 2	7 ± 1	5.0 ± 1.0	2.0 ± 1.0
RP/30.0	39 ± 4	27 ± 3	12 ± 2	5.0 ± 1.0	2.0 ± 1.0
RP/40.3	46 ± 4	33 ± 3	13 ± 2	5.6 ± 0.9	3.0 ± 1.0
RP/47.8	46 ± 4	32 ± 3	14 ± 2	4.8 ± 0.9	3.3 ± 0.7
122/53	21 ± 3	7 ± 1	5 ± 1	0.8 ± 0.2	2.9 ± 0.5
122/60	19 ± 2	5 ± 1	5 ± 1	1.7 ± 0.5	3.3 ± 0.7
120/38	48 ± 3	22 ± 2	9 ± 1	1.4 ± 0.5	5.2 ± 0.6
120/66	54 ± 3	29 ± 2	11 ± 1	3.3 ± 0.6	1.1 ± 0.6
1/32	22 ± 3	6 ± 1	6 ± 1	0.9 ± 0.4	3.5 ± 0.7
1/38	31 ± 3	13 ± 2	5 ± 1	1.2 ± 0.3	4.3 ± 0.8
1/53	42 ± 3	17 ± 2	8 ± 1	2.5 ± 0.5	5.4 ± 0.9
1/66	38 ± 3	16 ± 2	8 ± 1	1.5 ± 0.4	3.8 ± 0.5
1/72	33 ± 3	12 ± 1	7 ± 1	1.3 ± 0.4	4.6 ± 0.8
7/32	30 ± 3	9 ± 1	8 ± 1	1.2 ± 0.3	3.6 ± 0.7
7/38	24 ± 3	9 ± 1	4 ± 1	1.2 ± 0.3	4.4 ± 0.6
7/53	43 ± 3	15 ± 2	9 ± 1	2.2 ± 0.9	6 ± 1
7/44	43 ± 3	18 ± 2	8 ± 1	1.7 ± 0.5	6.0 ± 0.6
7/60	38 ± 3	17 ± 2	8 ± 1	1.5 ± 0.4	4.1 ± 0.5
7/66	24 ± 3	9 ± 1	4 ± 1	1.2 ± 0.3	3.2 ± 0.5
7/72	34 ± 3	11 ± 1	9 ± 1	1.7 ± 0.4	3.7 ± 0.8

SC	Fe	$Fe^{3+}(I)$	$Fe^{3+}(II)$	Fe^{2+}	Hem
13/32	13 ± 2	5 ± 1	3 ± 1	0.7 ± 0.2	1.5 ± 0.4
13/38	30 ± 3	13 ± 2	5 ± 1	1.8 ± 0.6	3.9 ± 0.7
13/44	32 ± 3	11 ± 1	7 ± 1	1.6 ± 0.4	3.5 ± 0.5
13/60	22 ± 3	6 ± 1	6 ± 1	1.1 ± 0.5	3 ± 1
13/66	47 ± 3	22 ± 2	8 ± 1	1.9 ± 0.5	5.2 ± 0.6
13/72	36 ± 3	12 ± 1	11 ± 1	1.4 ± 0.4	3.6 ± 0.5
19/32	30 ± 3	10 ± 1	10 ± 1	1.2 ± 0.4	3.3 ± 0.5
19/38	48 ± 3	17 ± 2	12 ± 2	1.9 ± 0.5	5.3 ± 0.6
19/44	32 ± 3	12 ± 1	6 ± 1	1.3 ± 0.4	3.9 ± 0.5
19/53	40 ± 3	16 ± 2	8 ± 1	1.6 ± 0.4	4.4 ± 0.5
19/60	34 ± 3	11 ± 2	9 ± 1	1.7 ± 0.4	4.1 ± 0.6
19/66	55 ± 3	23 ± 2	11 ± 1	2.2 ± 0.6	7.1 ± 0.7
19/72	25 ± 3	9 ± 1	7 ± 1	1.2 ± 0.3	3.5 ± 0.5
25/32	20 ± 3	9 ± 1	4 ± 1	0.8 ± 0.2	2.2 ± 0.4
25/38	54 ± 3	21 ± 2	11 ± 1	2.2 ± 0.6	8.0 ± 1.0
25/44	47 ± 3	19 ± 2	8 ± 1	2.4 ± 0.5	5.7 ± 0.6
25/53	10 ± 2	3 ± 1	3 ± 1	0.5 ± 0.1	1.4 ± 0.5
25/60	40 ± 3	16 ± 2	6 ± 1	2.0 ± 0.4	6.0 ± 0.9
25/66	45 ± 4	19 ± 2	9 ± 1	2.3 ± 0.5	5.9 ± 0.6
25/72	27 ± 3	9 ± 1	7 ± 1	1.1 ± 0.3	3.3 ± 0.5
31/32	34 ± 3	13 ± 2	8 ± 1	1.4 ± 0.4	4.4 ± 0.5
31/38	25 ± 3	10 ± 1	5 ± 1	0.8 ± 0.2	2.5 ± 0.4
31/44	33 ± 3	14 ± 2	7 ± 1	1.3 ± 0.4	3.0 ± 0.5
31/53	44 ± 4	18 ± 2	8 ± 1	2.2 ± 0.5	6.0 ± 0.8
31/60	47 ± 4	19 ± 2	10 ± 1	1.9 ± 0.5	4.7 ± 0.6
31/66	36 ± 3	12 ± 2	7 ± 1	2.1 ± 0.4	4.3 ± 0.5
31/72	33 ± 3	12 ± 2	8 ± 1	2.0 ± 0.7	3.6 ± 0.5
B1	44 ± 3	19 ± 2	7 ± 1	1.7 ± 0.5	6.1 ± 0.6
B2	36 ± 3	16 ± 2	5 ± 1	1.5 ± 0.4	5.8 ± 0.7
B3	32 ± 3	14 ± 2	6 ± 1	1.0 ± 0.3	3.9 ± 0.5

Table 3

Pearson correlation coefficients between total fractions of Fe phases and the radionuclides activity values. NS means not significant correlation. The subscript values show the correlation coefficients between Mössbauer relative fractions of Fe phases and the activity values presented in Montes et al. (2012).

	^{226}Ra	^{232}Th	^{40}K
Hematite	$-0.393_{(-0.510)}$	$NS_{(-0.790)}$	$-0.326_{(-0.63)}$
$Fe^{3+}(I)$	$0.629_{(0.270)}$	$0.580_{(0.842)}$	$0.771_{(0.640)}$
$Fe^{3+}(II)$	$0.611_{(0.180)}$	$0.588_{(0.495)}$	$0.739_{(0.102)}$
Fe^{2+}	$0.726_{(0.180)}$	$0.473_{(0.094)}$	$0.792_{(0.233)}$

Therefore, the significant and positive correlation obtained between total fractions of Fe^{2+} and the ^{40}K activity values should be attributed to the existence of a significant and positive correlation between illite and ^{40}K activity, in agreement with the result reported by Popov et al. (2011) and Sawney (1969). The present significant and positive correlation is a consequence of considering the Fe^{2+} total fraction and it could not be deduced if only the Mössbauer relative fraction of Fe^{2+} is taking into account.

4. Conclusions

In the frame of this work an approximate new methodology has been developed for the determination of the total content of Fe in soils as a simple and non-destructive technique, based on Mössbauer results. The method was successfully applied in soils with Fe contents from 25 g/kg to about 110 g/kg. Analysis of samples with Fe concentration higher than 110 g/kg is possible if diluted samples are used, giving *IAA* value lying in the linear region. This novel methodology was successfully applied to determining Fe concentrations in soils of Buenos Aires Province, Argentina with an accuracy of 15%.

Pearson correlation coefficients between total Fe phase content and ^{40}K, ^{226}Ra and ^{232}Th activities were calculated for soils of the Province of Buenos Aires, Argentina. These coefficients show differences with those previously reported, which were calculated using the Mössbauer Fe-phases relative fractions.

The new coefficient values show that the correlation between hematite and the ^{226}Ra and ^{40}K is weak, other studies are necessary to reach a significant conclusion. Correlation between Fe^{3+} total fractions and ^{226}Ra, ^{232}Th and ^{40}K activity values resulted significant and positive. In the case of ^{226}Ra, the result is now more representative than that obtained before due to the fact that ^{226}Ra can interact strongly with clay minerals.

Fe^{2+} total fraction and ^{40}K activity values showed a significant and positive correlation coefficient. Because of Fe^{2+} concentration was principally associated to the illite mineral, this result indicated that, ^{40}K interacts with this clay mineral, as it is known from batch experiments. This very important conclusion cannot be observed when only the Mössbauer relative fraction of Fe^{2+} was considered.

Fig. 2. ^{40}K vs Fe^{2+} content. Data of the linear fitting are also presented.

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