CrossMark

Determination of the self-attenuation based on the sample composition in gamma-ray spectrometry of ^{210}Pb: requirements for the scope of chemical analyses

Paweł Jodłowski[1] · Przemysław Wachniew[1] · Jakub Nowak[1]

Abstract In the presented paper analysis of sensitivity of self-attenuation correction C_s to the accuracy of chemical composition analysis is presented. The analyses were done by means of Monte Carlo simulation for cylindrical samples and for four sample materials: peat, water, ash and soil. For each of these materials the major elements were selected whose determination in the analysed material is necessary. For the remaining elements threshold levels of their concentration were determined—if expected element concentration in a sample exceeds this value, its determination is indispensable, assuming the accuracy of C_s determination at 3 %.

Keywords Gamma-ray spectrometry · Self-attenuation · ^{210}Pb · Chemical composition · Monte Carlo simulation

Introduction

Naturally occurring radionuclide ^{210}Pb is commonly used in studies of processes associated with sediment accumulation in surface water bodies, river valleys and hill slopes. The most common application of ^{210}Pb is connected with determination of sediment age and tracing of eroded soils and sediments. Gamma-ray spectrometry method enables accurate ^{210}Pb determination but the key issue for measurement accuracy, especially for low-energy radiation emitted by ^{210}Pb (46.5 keV), is determination of self-

attenuation correction accounting for photon attenuation in volume sample. If the sample and the standard are handled in the same geometric setup this correction with respect to the standard (calibration source) is evaluated as a ratio of the detector efficiency for the standard ε_c to the detector efficiency for the sample ε_s:

$$C_s(E) = \frac{\varepsilon_c}{\varepsilon_s}. \qquad (1)$$

The C_s correction is significant for measurements of low energy gamma radiation. In such cases its determination is particularly troublesome (cf. [1]). This difficulty stems from the fact that the mass attenuation coefficient for low energies differs considerably between elements, therefore the impact of the chemical composition on attenuation properties of the material studied is decisive.

Two practical approaches have been developed to cope with that problem. The C_s correction is either determined experimentally or calculated on the basis of the known chemical composition and density of the material.

Usually the transmission method proposed by Cutshall [2] is used for the experimental evaluation of C_s. This method combines the values of the linear attenuation coefficient obtained by the transmission measurement with the so-called self-attenuation equation for cylindrical samples. However, the simplified formula used in this method is questioned by many authors who observed that its application leads to systematic errors and proposed modifications [3–5].

As advanced methods of chemical analyses (e.g. fluorescence analysis, mass spectrometry) have become more widely available, some papers confirm the viability of evaluating the C_s correction based on sample chemical composition [6–8]. Methods used in computing the C_s correction on the basis of the chemical composition

✉ Paweł Jodłowski
  jodlowski@fis.agh.edu.pl

[1] Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland

🙋 Springer

include: application of self-attenuation equation, the Debertin method [9] and Monte Carlo simulations.

In this paper the analysis of sensitivity of C_s estimation to the accuracy of chemical composition analysis is presented. In order to determine C_s correction it is necessary to know the chemical composition of the analysed sample, however, there is no need to determine all elements in a sample. The aim of this work is to identify the minimal scope of chemical analyses and the particular elements whose determination is indispensable.

Experimental

In order to evaluate sensitivity of self-attenuation correction C_s to the accuracy of chemical composition analysis the ratio C_s/C_{s0} was determined for different elements, where C_{s0} is the self-attenuation correction for a given material (e.g. peat—Fe concentration 5 %, cf. Table 1) and C_s is correction for the same material with a different concentration of this element (e.g. 6 % Fe). The C_s/C_{s0} ratio equals

$$\frac{C_s(E)}{C_{s0}(E)} = \frac{\varepsilon_c/\varepsilon_s}{\varepsilon_c/\varepsilon_{s0}} = \frac{\varepsilon_{s0}}{\varepsilon_s}, \tag{2}$$

where ε_{s0} is detector efficiency for the given material and ε_s is efficiency for the same material with different concentration of the element. As can be seen from (2), value of C_s/C_{s0} does not depend on the detector efficiency for the material of the standard (cf. Eq. 1).

The basic calculations of the C_s/C_{s0} values were performed with Monte Carlo (MC) method; MCNP4C code was used [10]. The MC method provided values of the detector efficiencies ε_{s0} and ε_s from which C_s/C_{s0} was calculated using Eq. (2). The simulations were performed for the 46.54 keV photons emitted by ^{210}Pb. The spectrometric setup [11] for which the calculations were performed comprised a semiconductor detector HPGe (Canberra GX4020) with the resolution 1.9 keV, energy range above 3 keV and relative efficiency 42 %. The detector has a cylindrical shape with the diameter of 6.1 cm and the height of 6.0 cm; the distance between the detector crystal and the 0.5 mm carbon composite window of detector equals 0.6 cm. The detector is covered during measurements with a hood-shaped 1.4 mm thick Teflon protection cap, placed above the detector window; the distance between the detector crystal and the sample is 0.81 cm. The detector is placed in a shielding made of lead bricks 10 cm thick with a 1 mm cadmium and 1 mm copper inner lining.

The simulations were done for the specific measuring geometry where sample containers covered with a cap were positioned axially, directly on the detector. The polystyrene container walls have the density 1.05 g/cm^3 and the

Table 1 Threshold concentrations for the studied materials and elements

		Peat[a] $\mu_l = 0.1300$[e] $C_s = 0.880$[f]	Water[b] $\mu_l = 0.2378$ $C_s = 1.000$	Ash[c] $\mu_l = 0.5129$ $C_s = 1.344$	Soil[d] $\mu_l = 0.6242$ $C_s = 1.486$
C	$\mu_m = 0.1927$[e]	MajEl (60 %)	60 % (0 %)	25 % (0 %)	20 % (1 %)
O	$\mu_m = 0.2251$	MajEl (18 %)	MajEl (89 %)	MajEl (48 %)	MajEl (50 %)
Al	$\mu_m = 0.4188$	45 % (3 %)	15 % (0 %)	40 % (13 %)	35 % (7 %)
Si	$\mu_m = 0.5049$	MajEl (12 %)	10 % (0 %)	MajEl (21 %)	MajEl (34 %)
Ca, K	$\mu_m = 1.224$[g]	9 % (2 %)	2.5 % (0 %)	11 % (7 %)	4 % (1 %)
Fe	$\mu_m = 2.382$	7 % (5 %)	1.1 % (0 %)	7 % (5 %)	5 % (4 %)
Pb	$\mu_m = 9.682$	0.7 % (0 %)	0.25 % (0 %)	0.3 % (0 %)	0.25 % (0 %)

Threshold values in italics concern elements whose determination in the analyzed material is necessary if the expected element concentration in a sample exceeds threshold value and the underlined threshold values concern elements whose determination is not necessary. Numbers in brackets represent the baseline concentrations of elements (details cf. section "Experimental")

MajEl major elements

[a] Exemplary peat; chemical composition: 60 % C, 18.5 % O, 11.5 % Si, 5 % Fe, 3 % Al, 2 % Ca; density 0.35 g/cm^3

[b] Water; density 1.00 g/cm^3

[c] Typical ash; chemical composition: 47.9 % O, 20.7 % Si, 12.9 % Al, 7.4 % Ca, 5.3 % Fe, 3.2 % Mg, 2.6 % S; density 1.0 g/cm^3

[d] "Average" soil; chemical composition: 50 % O, 34 % Si, 7 % Al, 4 % Fe, 1 % C, 1 % Ca, 1 % K, 0.7 % Na, 0.6 % Mg, 0.5 % Ti, 0.1 % N, 0.1 % P; density 1.4 g/cm^3 [16]

[e] μ_m, μ_l—mass (cm^2/g) and linear (1/cm) attenuation coefficient at 46.54 keV [17]

[f] Self-attenuation correction with respect to the water standard (calibration source) is provided to show the scale of self-attenuation effect and is not discussed in the text [g] μ_m for Ca
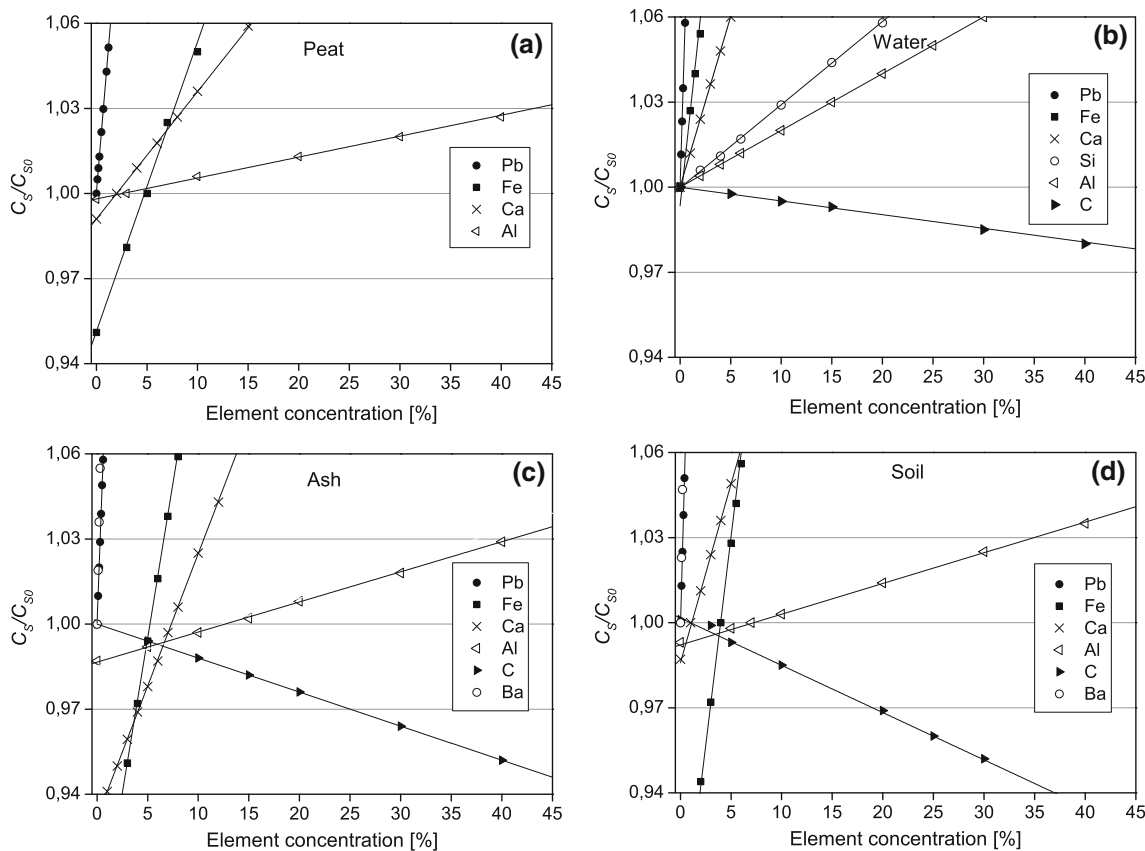
Fig. 1 C_s/C_{s0} vs. element concentration for peat (**a**), water (**b**), ash (**c**) and soil (**d**). The threshold concentration is defined by the C_s/C_{s0} ratios equal to 1.03 or 0.97. *Fitting lines* are plotted for clarity

thickness 1 mm. Sample volume is 84.8 cm³ with diameter of 6.0 cm, and height of 3.0 cm which is a typical thickness for environmental samples.

The C_s/C_{s0} as a ratio of efficiencies (cf. Eq. 2) is little sensitive to detector model [12, 13]. Therefore, the calculations were performed for nominal detector dimensions provided by the manufacturer. The time of calculations was chosen in order to keep the type A uncertainty [14] of the calculation results less than 0.1 %.

The input data for the computations included the geometry of the measurement and the chemical composition and density of a sample. The simulations were done for four sample natural materials (matrices) with different densities and chemical compositions: peat, water, ash and soil (cf. footnotes to Table 1).

An exemplary calculation procedure is described below for peat (chemical composition: 60 % C, 18.5 % O, 11.5 % Si, 5 % Fe, 3 % Al and 2 % Ca) and element Fe.

1. C_{s0} calculations for the above-mentioned baseline peat composition,
2. C_s calculations for peats with Fe concentration changing from 0 to 10 %. In order to compensate for the change in Fe concentration concentrations of the major peat

components (C, O, Si) had to be modified proportionally to their original concentrations so that their sum remained equal to 100 %. Concentrations of minor components were not changed. For example, the resulting peat composition for Fe concentration 6 % was: 59.3 % C, 18.3 % O, 11.4 % Si, 6 % Fe, 3 % Al and 2 % Ca.

3. Determination of the relationship between Fe concentration in peat and C_s/C_{s0} value (cf. Fig. 1).

The above calculations were performed for the reference spectrometric setup (detector efficiency 42 %, sample diameter *d* 6.0 cm, sample height *h* 3.0 cm, sample density *ρ* 1.0 g/ccm; coded as GX40_d60h30_ρ1.0). In order to evaluate the applicability range of the obtained results, in particular of the threshold values for element concentrations, additional calculations were performed for ash measured in other spectrometric setups (cf. Table 2):

- detectors with the crystal diameters 4.8, 6.1 and 7.6 cm (relative efficiency about 20, 42 and 80 %, respectively—cf. formula in [15], the end-cap diameters 7.6, 7.6 and 9.5, respectively); MCNP models of these detectors are based on MCNP model of GX4020 detector,

Table 2 Threshold element concentration for ash and for different spectrometric setups

	GX40_ d60h30_ρ1.0	GX40_ d20h30_ρ1.0	GX40_ d100h30_ρ1.0	GX40_ d60h10_ρ1.0	GX40_ d60h40_ρ1.0	GX20_ d60h30_ρ1.0	GX80_ d60h30_ρ1.0	GX40_ d60h30_ρ0.5	GX40_ d60h30_ρ1.5	GX40_ d60h40_ρ2.0
C	24 % (0 %)	33 %	21 %	50 %	22 %	25 %	24 %	43 %	20 %	17 %
O	MajEl (48 %)	MajEl	MajEl	MajEl	MajEl	MajEl	MajEl	MajEl	MajEl	MajEl
Al	41 % (13 %)	50 %	38 %	67 %	39 %	42 %	41 %	60 %	35 %	32 %
Si	MajEl (21 %)	MajEl	MajEl	MajEl	MajEl	MajEl	MajEl	MajEl	MajEl	MajEl
Ca, K	10.6 % (7 %)	11.7 %	10.3 %	13.5 %	10.3 %	10.8 %	10.6 %	13.0 %	9.9 %	9.6 %
Fe	6.7 % (5 %)	7.1 %	6.5 %	8.0 %	6.6 %	6.8 %	6.6 %	7.6 %	6.4 %	6.2 %
Pb	0.31 % (0 %)	0.42 %	0.27 %	0.60 %	0.29 %	0.34 %	0.31 %	0.53 %	0.24 %	0.22 %

Explanation of symbols and abbreviations cf. Table 1

[a] GX20, GX40, GX80—detector with the relative efficiency 20, 42, 80 %, respectively
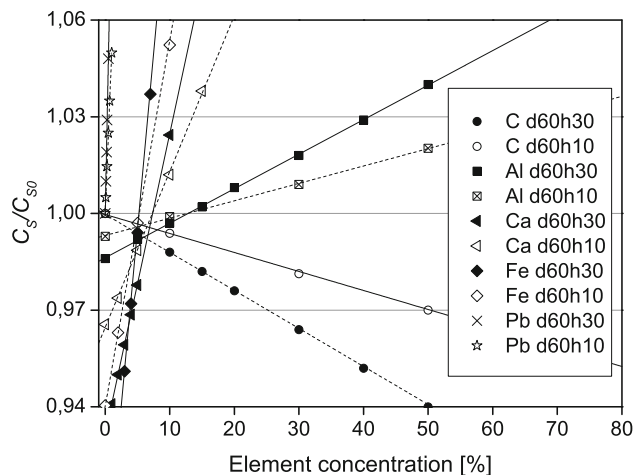
Fig. 2 C_s/C_{s0} vs. element concentration for ash and two different spectrometric setup: GX40_d60h30_ρ1.0 and GX40_d60h10_ρ1.0

- sample diameters d 2.0 and 10.0 cm,
- sample heights h 1.0 and 4.0 cm,
- sample densities ρ 0.50, 1.5 and 2.0 g/ccm.

Results and discussion

The relationships between element concentrations and C_s/C_{s0} for the peat, water, ash and soil are presented in Fig. 1a–d. Slopes of the regression lines are the measure of sensitivity of self-attenuation correction C_s to changing concentrations of different elements.

Three groups of elements were identified:

- major elements, determination of their concentrations in the analysed material is indispensable (e.g. C, O and Si for peat),
- elements whose determination in the analysed material is necessary when the expected element concentration in a sample exceeds threshold value; in some cases (see Fe below) also a lower threshold can be defined,
- elements whose determination in the analysed material is not necessary because the threshold concentration is significantly different from the expected concentration of an element in the studied material.

We understand the threshold concentration as the concentration of an element in a sample for which the error of C_s resulting from assuming average concentration of this element in the analysed material, exceeds the maximum acceptable uncertainty. For the maximum acceptable uncertainty of 3 % assumed in this work the threshold values are defined by $C_s/C_{s0} = 1.03$ or $C_s/C_{s0} = 0.97$ (cf. Fig. 1).

Table 1 shows classification of the elements and their respective threshold concentrations for the considered materials. E.g. for soil samples:

- Si and O are major elements,
- threshold concentration of Ca, K, Fe equals 4, 4 and 5 %, respectively, whereas concentration of these elements in soil equals 1, 1 and 4 %, respectively. Thus, it is necessary do determine Ca, K and Fe concentrations. Iron is a specific case as two threshold concentrations can be defined, for $C_s/C_{s0} = 0.97$ and $C_s/C_{s0} = 1.03$,
- threshold concentration of Al and Pb equal 35 and 0.25 %, respectively, whereas concentration of these elements in soil is significantly lower and equals 7 and 0 %, respectively. Thus, it is not required to determine Al and Pb concentrations,
- threshold concentration of C equals 20 %, whereas concentration of this element in considered soil equals 1 %. Thus, it is required to determine C concentration only for organic soils.

One has to note that for materials of industrial origin also other elements with concentrations exceeding the environmental levels have to be considered. For example, Ba concentrations in drilling wastes reach up to several percent while the threshold concentration estimated for a typical drilling waste is at a fraction of a percent (cf. Fig. 1c–d).

Results of calculations aiming at determination of applicability range for the obtained threshold values are presented in Fig. 2 and Table 2. Figure 2 shows C_s/C_{s0} values for the reference setup (GX40_d60h30_ρ1.0) and for the setup GX40_d60h10_ρ1.0, that revealed the largest discrepancies from the reference setup. As can be seen, the C_s/C_{s0} for these geometries (and for other analysed setups too) differ by less than 1.5 % for the C_s/C_{s0} values for reference setup from the range 0.97–1.03 and reach up to 3 % for the C_s/C_{s0} values from the ranges 0.94–0.97 and 1.03–1.06. The relative differences of the threshold concentrations between most spectrometric setups do not exceed 20 % (cf. Table 2). Only for the setups GX40_d60h10_ρ1.0 and GX40_d60h30_ρ0.5, for which absorption is significantly smaller than for the reference setup, the C_s/C_{s0} values are overestimated by a few tens of percent.

A crucial, for the applicability of the basic calculations, factor is whether classification of a particular element to one of the three groups (cf. "Results and discussion" section) is the same for different setups. For example, as can be seen from Table 2 classification for ash is the same for all setups, i.e. Ca, K and Fe have to be determined while there is no need to determine Al and Pb.

Conclusions

Sensitivity of self-attenuation correction C_s to the accuracy of chemical composition analysis was evaluated. The analyses were done by means of Monte Carlo simulation method for a cylindrical samples with 3 cm in height, 6 cm in diameter and for four types of environmental materials: peat, water, ash and soil. For each of these materials the major elements were selected whose determination in the analysed material is necessary. For the remaining elements that often occur in environmental samples, threshold levels of their concentration were determined—if the expected element concentration in a sample exceeds this value, its determination is indispensable, assuming the accuracy of C_s determination at 3 %. The applicability range of the obtained results, in particular of the threshold values for element concentrations, was evaluated.

The results presented in the paper help to limit the scope of chemical analyses in measurements of ^{210}Pb activity by gamma-spectrometry to those elements that are essential for correct determination of C_s correction. A proper selection of the elements leads to the reduction of time and resources necessary for a reliable determination of ^{210}Pb in environmental samples.

References

1. Jodłowski P (2006) Self-absorption correction in gamma-ray spectrometry of environmental samples—an overview of methods and correction values obtained for the selected geometries. Nukleonika 51(Suppl 2):S21–S22
2. Cutshall N, Larsen IL, Olsen CR (1983) Direct analysis of 210Pb in sediment samples: a self-absorption corrections. Nucl Instr Method Phys Res 206:309–312
3. McMahon CA, Fegan MF, Wong J et al (2004) A simplified technique to determine the self-absorption correction for sediment samples. Appl Radiat Isot 60:571–577
4. Pilleyre T, Sanzelle S, Miallier D, Faïn J, Courtine F (2006) Theoretical and experimental estimation of self-attenuation corrections in determination of ^{210}Pb by gamma-spectrometry with well Ge detector. Radiat Meas 41(3):323–329
5. Jodłowski P (2016) A revision factor to the Cutshall self-attenuation correction in ^{210}Pb gamma-spectrometry measurements. Appl Radiat Isot 109:566–569
6. San Miguel EG, Perez-Moreno JP, Bolivar JP, Garcia-Tenorio R, Martin JE (2002) ^{210}Pb determination by gamma spectrometry in voluminal samples (cylindrical geometry). Nucl Instr Method Phys Res A 493:111–120
7. Saidou, Bochud F, Laedermann JP, Buchillier T, Moise KN, Froidevaux P (2007) Calibration of an HPGe detector and self-attenuation correction for [210]Pb: verification by alpha

spectrometry of Po-210 in environmental samples. Nucl Instr Method Phys Res A 578:515–522

8. Villa M, Hurtado S, Manjón G, García-Tenorio R (2007) Calibration and measurement of ^{210}Pb using two independent techniques. Radiat Meas 42:1552–1560

9. Debertin K, Ren J (1989) Measurement of activity of radioactive samples in Marinelli beakers. Nucl Instr Method Phys Res A 278:541–549

10. X-5 Monte Carlo Team (2003) MCNP—version 5, Overview and Theory, vol I. LA-UR-03-1987, Los Alamos

11. Jodłowski P, Kalita SJ (2010) Gamma-ray spectrometry laboratory for high-precision measurements of radionuclide concentrations in environmental samples. Nukleonika 55(2):143–148

12. Jodłowski P (2007) Correction factors to account for minor sample height variations in gamma-ray spectrometry. Nucl Instr Method Phys Res A 580:238–241

13. Sima O, Dovlete C (1997) Matrix effects in the activity measurement of environmental samples implementation of specific corrections in a gamma-ray spectrometry analysis program. Appl Radiat Isot 48:59–69

14. JCGM 100 (2008) Evaluation of measurement data—guide to the expression of uncertainty in measurement. Joint Committee for Guides in Metrology

15. ORTEC Overview of Semiconductor Photon Detectors, ORTEC technical note, ORTEC, Oak Ridge, TN, USA. http://www.ortec-online.com/download/Overview-of-Semiconductor-Photon-Detectors.pdf. Accessed 10 June 2016

16. Vinogradov AP (1959) The geochemistry of rare and dispersed chemical elements in soils. Consultants Bureau Enterprises, New York

17. Berger MJ, Hubbell JH, Seltzer SM, Chang J et al (2010) XCOM: photon cross section database (version 1.5). National Institute of Standards and Technology, Gaithersburg. http://physics.nist.gov/xcom. Accessed 10 June 2016