Radioactivity analysis of ash from biomass power plants (BMKW/BMHKW)

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Content

Motivation

When biomass is burned, the non-combustible components of a large volume are concentrated in a small volume of ash. Large amounts of ashes from biomass power plants are usually used as additives for cement production.

Plants absorb dissolved radioactive substances from the soil through their nutrient cycle. This applies in particular to the easily soluble, naturally occurring radium isotopes of the uranium and thorium decay series, the potassium isotope K-40 and the cesium isotope Cs-137. As a result of the Chernobyl reactor accident, large amounts of Cs-137 were distributed primarily in northern, eastern and southern Europe and parts of Central Europe and stored in the upper soil layers. Due to its low mobility, the concentration decreases only very slowly. Some of the countries affected are among the largest European wood producers, so it must be assumed that large quantities of contaminated wood and wood waste are used as fuel.

With the cement, the radionuclides enter in the human environment in a concentrated form, e.g. as plaster and screed. The consequences are an increased local dose rate but also the emanation of radon. Measurements have shown that exceeding the legal radon reference value is due to radon emanation from cement products.

Due to the different origins of the biomass, the activities and ratios of the different isotopes in the ash are subject to strong fluctuations. A continuous and rapid test procedure is therefore required for controlled transfer. With the Lab-Scout, expensive and time-consuming laboratory analyzes can be replaced by a quick "on-site" measurement. This text shows the suitability of the method based on real samples.

Activity determination with the Lab-Scout

The Lab-Scout with the Lab-Scout Works operating software is an extremely easy-to-use measuring station for directly determining the weight-specific activity of material samples. The principle of gamma spectroscopy using a large-volume NaI scintillation detector with lead shielding allows samples to be evaluated safely, accurately and quickly with regard to the limit values to be observed. The measuring station can also be operated under field conditions without expert knowledge and with minimal maintenance effort. All calibration work can easily be carried out by yourself.

Three different analysis methods are available for determining the net count rates, which can be individually assigned to each of the emission lines selected for analysis. This enables optimization with regard to the uncertainty of the count rate determination and systematic deviations due to resolution-related overlapping of emission lines.

The measurement data can be stored in the device so that the samples can be measured one after the other even by untrained personnel. The measurement results are available for subsequent evaluation with a simple click of the mouse, since all the necessary analysis settings for a sample type are saved. Special knowledge is not required.

fig. 1 - Lab Scout with wood pellets probe

Analyzed nuclides

Cs-137

The only significant emission line of Cs-137 at 662 keV is partially superimposed by the 609 keV emission line of the radium progeny Bi-214 due to the characteristics of NaI detectors. Both lines generate a so-called doublet in the spectrum, which is resolved by a mathematical unfolding.

K-40

A sufficiently isolated emission line with a high transition probability at 1463 keV is available for the potassium isotope K-40. Only faint lines from Ac-228 (Th-232 series) and Bi-214 (U-238 series) overlap the energy range of the K-40 peak.

Ra-228 and Th-228 (Th-232 series)

The secondary product Tl-208 can be used to determine the activity of Th-228. This has a sufficiently strong emission line at 2614 keV. In addition, there is no significant background from other isotopes in this energy range. Whether an equilibrium between Ra-228 and Th-228 can be assumed depends strongly on the sample, since both isotopes have different mobility due to their different solubility. In the case of wood that has grown over many years, both values should be close together due to the half-lives, as the analyzed samples also show. The activity is mainly absorbed via the easily soluble isotope Ra-228 from which Th-228 is generated. The escape of activity by the gaseous isotope Rn-220 (in the decay chain before Th-208) is prevented by a closed sample cup. Due to the short half-life of approx. one minute, diffusion is negligible even with plastic cups. However, after filling and sealing the sample container, the sample should be stored for 48 hours. The radioactive balance, which may have been disturbed by Rn-220 emanation before sample closure, is restored after 4 to 5 half-lives of Pb-212 (approx. 11 h).

Ra-226 (U-238 series)

Ra-226 can also only be determined indirectly via the decomposition product Bi-214. The well isolated emission line at 1764 keV is suitable for this. This is amplified by another line at 1729 keV. A slight superimposition is only given by an emission line of Bi-212 (Th-232 series) at 1621 keV. Due to the more than ten times lower probability of transition, however, there is only an influence in the case of Th-228 activities that are greatly increased in comparison to Ra-226. The treatment of the sample plays an important role in the measurement. The noble gas Rn-222, which is in the decay chain before the Bi-214 used for the analysis, has a sufficiently long half-life of just under four days to escape from the sample. A significant emanation of Rn-222 is to be expected for fly ash with a particle surface that is comparatively large in relation to the particle volume. After the sample has been sealed gas-tight, the analysis must be delayed for at least 16 to 20 days. After that, radioactive equilibrium is established via Rn-222. When using plastic vessels, a loss of Rn-222 through diffusion is to be expected despite careful sealing.

Analysis methodology

The device software Lab-Scout Works provides three different calculation methods for determining the net count rates of the emission lines. The selection was made using the scheme specified in the manual according to the prerequisites and requirements presented there. The trapezoidal method was used for the isolated lines of Bi-214 (1764 keV), Tl-208 (2614 keV) and K-40, while Cs-137 and the 609 keV line of Bi-214 form a doublet, which is replaced by Doublet - unfolding is analyzed. Since K-40 and the isotopes of the Th-232 and U-238 decay series are also present in the vicinity of the measuring station and complete shielding by a lead jacket is impossible, a background spectrum acquired before the actual measurement is subtracted from the sample spectrum.

The weight of the samples is determined by the integrated scales of the Lab-Scout. The weight of the sample container is automatically subtracted by prior taring. The displayed weight-specific activity is calculated from the quotient of the determined activity and the net sample weight.

Analyzed Samples

To verify the procedure, five fly ash samples were taken from the production process of a biomass power plant. The samples contain different amounts of Cs-137, K-40, Ra-226 and Ra-228. All samples were measured by a laboratory according to ISO 17025 with an HPGe detector. The measurement time was 16 hours in each case. The table below shows the results of the laboratory analysis.

Isotop	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Cs-137 [Bq]	421 ± 33	156 ± 13	239 ± 19	79 ± 6,4	68 ± 5,5
K-40 [Bq]	1340 ± 100	918 ± 80	1410 ± 120	1430 ± 120	1760 ± 150
Ra-226 [Bq]	38 ± 2,5	97 ± 4,6	65 ± 3,6	84 ± 4,3	66 ± 3,8
Ra-228 [Bq]	58 ± 2,6	64 ± 3,2	64 ± 3,3	66 ± 3	81 ± 2,9
Th-228 [Bq]	62 ± 3,4	61 ± 4	59 ± 4,2	61 ± 3,8	77 ± 4,4

Marinelli beakers of type ISOTRAK NQ7013 with a nominal capacity of one liter and Schapp closure were used for all samples. The actual volume of the sample containers was slightly less than one liter. This could be due to compaction caused by the shipment of the samples by courier service.

To obtain the weight-specific activity, the determined activity is divided by the net weight of the sample:

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Netto-weight[kg]	0,86	0,76	0,87	0,87	0,86
Cs-137 [Bq/kg]	490 ± 38	205 ± 17	275 ± 22	90 ± 7,4	79 ± 6,4
K-40 [Bq/kg]	1558 ± 116	1208 ± 105	1621 ± 120	1644 ± 159	2046 ± 174
Ra-226 [Bq/kg]	44 ± 2,5	128 ± 6	75 ± 4,1	96 ± 4,9	77 ± 4,4
Ra-228 [Bq/kg]	67 ± 3,4	84 ± 4,2	74 ± 3,8	76 ± 3,5	94 ± 3,4
Th-228 [Bq/kg]	72 ± 4	80 ± 5,3	68 ± 4,8	70 ± 4,4	90 ± 5,1

Furthermore, two samples with wood pellets in the identical Marinelli beaker were examined, the activities of which are one to two orders of magnitude lower than those of the ash samples. The Cs-137 activity of sample 6 was determined by the laboratory to be weight-corrected at 6.9 ± 0.75 Bq/kg and that of sample 7 at 0.7 ± 0.24 Bq/kg.

Calibration of the Lab Scout

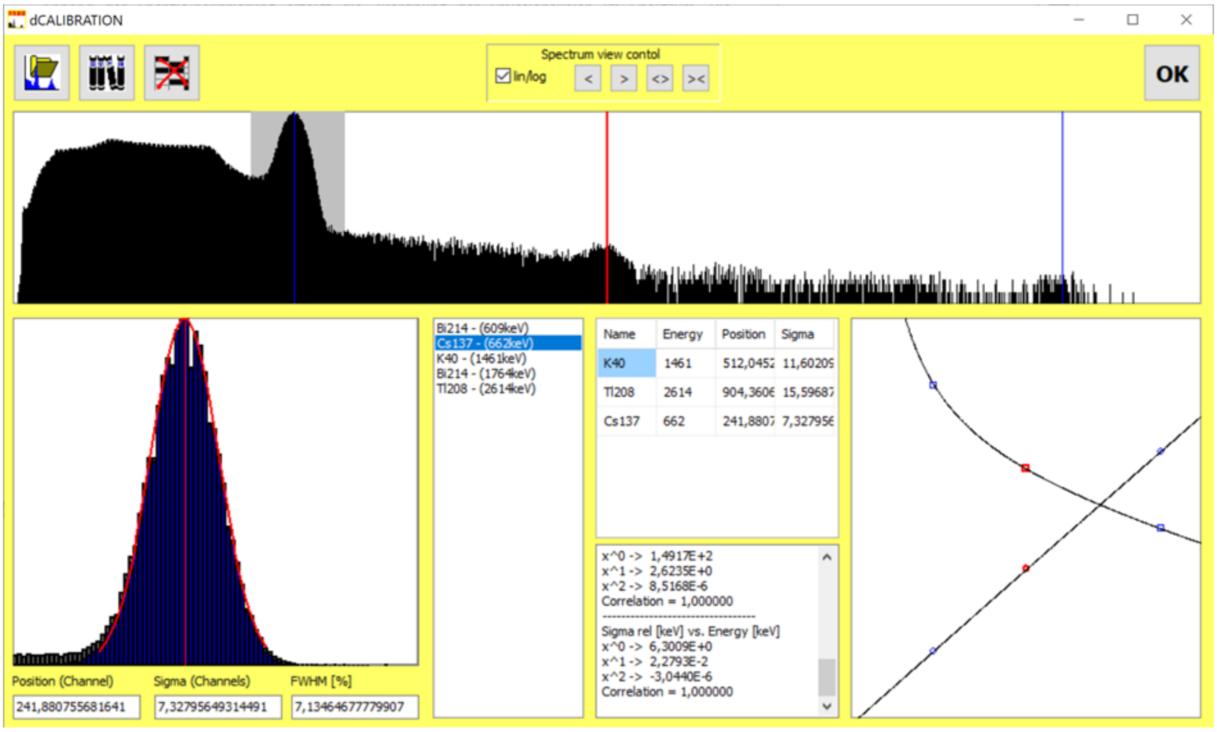
Appropriate assistants, which are described in detail in the device manual, are available in Lab-Scout Works for the necessary calibrations. All calibrations must be carefully performed and the results obtained verified.

Energy and peak width calibration

The emission lines in the spectrum are assigned based on the energy calibration. The peak width calibration defines the shape of the emission line expected at any position in the spectrum. The shape is used to verify the emission line and ensure correct doublet modelling. For best results, it is recommended to use sources with a small number (possibly only one) of emission lines. These should either contain the later used for analysis or energetically close lines. In the case of the measurement considered here, this is easily possible:

- Cs-137; Spot emitter 10kBq (662 keV)
- K-40; Marinelli beaker filled with potassium permanganate (1461 keV)
- Tl-208; Thorium mantle (2614 keV)

A spectrum was acquired for each of the three sources and the calibration points were transferred one after the other to the Lab-Scout Works calibration assistant. The spectrum of the Cs-137 source can be seen in the figure below as an example. The also visible K-40 and Tl-208 lines result from background radiation.



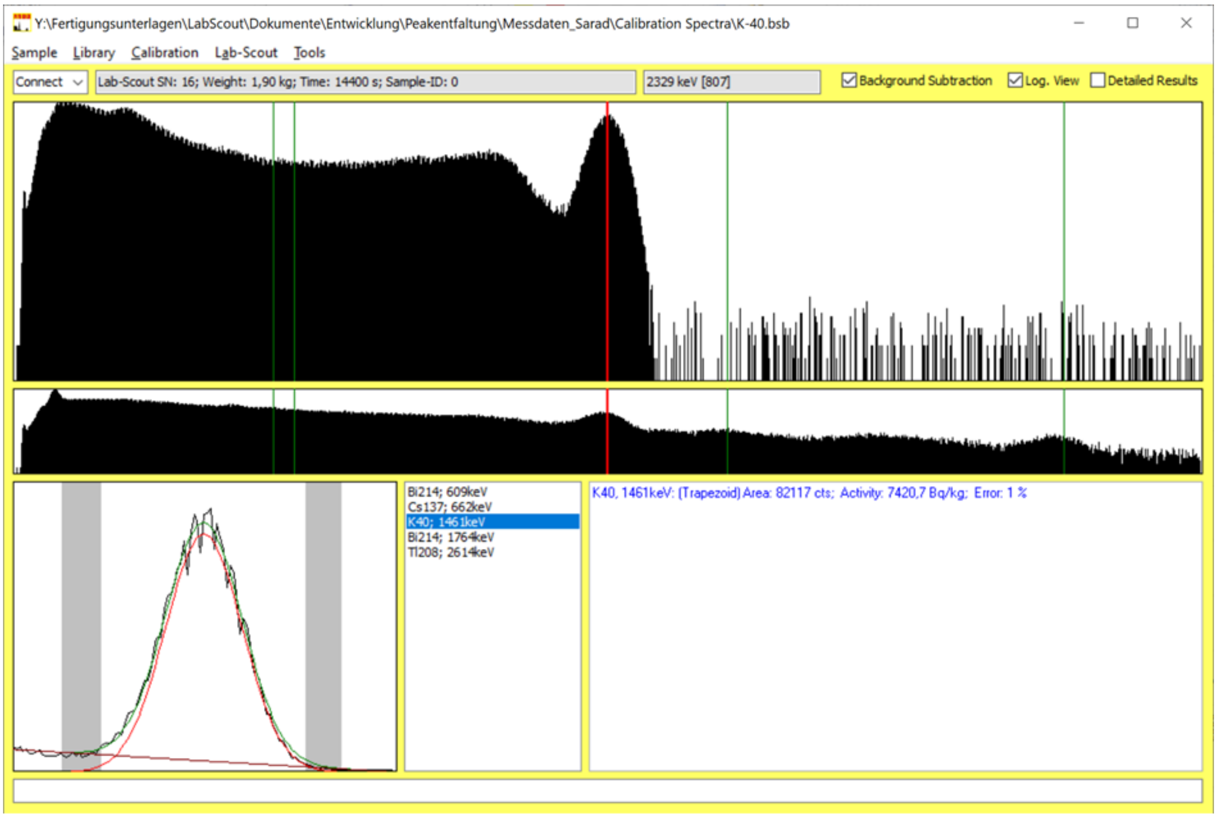
Bi214 - (609keV)
Cs137 - (662keV)
K40 - (1461keV)
Bi214 - (1764keV)
Tl208 - (2614keV)

Name	Energy	Position	Sigma
K40	1461	512,0452	11,60209
Tl208	2614	904,3606	15,59687
Cs137	662	241,8807	7,327956

```
x^0 -> 1,4917E+2
x^1 -> 2,6235E+0
x^2 -> 8,5168E-6
Correlation = 1,000000
--------------------------------
Sigma rel [keV] vs. Energy [keV]
x^0 -> 6,3009E+0
x^1 -> 2,2793E-2
x^2 -> -3,0440E-6
Correlation = 1,000000
```

Position (Channel): 241,880755681641
Sigma (Channels): 7,32795649314491
FWHM [%]: 7,13464677779907

The respective peak widths are determined interactively with the assistant (device manual) and should be checked visually using the trapezoidal analysis. The figure below shows a good fit of the peak shape determined by means of peak width calibration to the measured spectrum (bottom left in figure).



Y:\Fertigungsunterlagen\LabScout\Dokumente\Entwicklung\Peakentfaltung\Messdaten_Sarad\Calibration Spectra\K-40.bsb

Lab-Scout SN: 16; Weight: 1,90 kg; Time: 14400 s; Sample-ID: 0

2329 keV [807]

☑ Background Subtraction ☑ Log. View ☐ Detailed Results

Bi214; 609keV
Cs137; 662keV
K40; 1461keV
Bi214; 1764keV
Tl208; 2614keV

K40, 1461keV: (Trapezoid) Area: 82117 cts; Activity: 7420,7 Bq/kg; Error: 1 %

Efficiency calibration

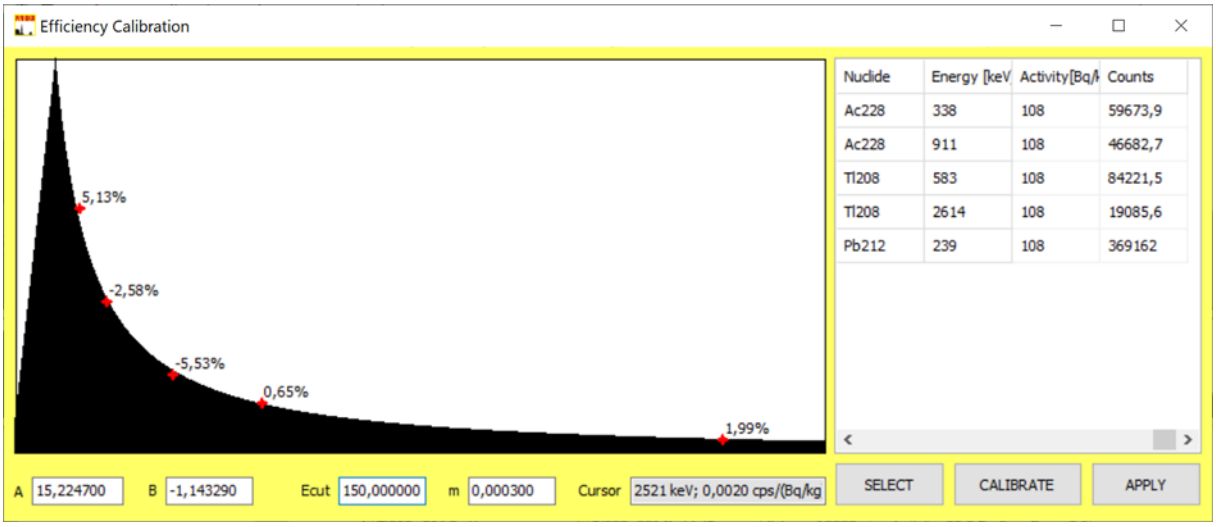
The efficiency calibration assigns the corresponding activity to the measured count rate of an emission line. The efficiency (better counting efficiency) of a detector depends on the energy of the emission line and the measurement geometry (sample container, filling quantity, density). Therefore, the sample geometry used for the efficiency calibration must correspond to the geometry used later. The energy dependence of the efficiency is described using a function whose shape parameters are determined using an adjustment to measured support points. The reference points are determined by measuring reference samples with known activity. For an optimal result, emission lines should be available as support points over the entire energy range. It is advantageous to use a reference sample with different lines in radioactive equilibrium. Using different reference samples reduces the accuracy of the fit due to the independent uncertainties in their nominal activity report. When selecting the lines, proceed according to the scheme given in the manual.

A uranium/thorium reference standard from Eckert & Ziegler, type QCRB22009 (SN: AK-5599), was used for the efficiency calibration. The sample is contained in an ISOTRAK NQ7013 Marinelli cup, like that used for the ash samples. The Th-232 decay series provides well-distributed emission lines in the range from 239 keV (Pb-212) to 2614 keV (Tl-208). Since the active material is embedded in a resin, emanation of Rn-220 can be ruled out. As a basis for the efficiency calibration, a spectrum of this sample was acquired with a measurement time of 48 hours. The previously acquired background spectrum was subtracted for the calibration (setting in Lab-Scout Works). The following emission lines with the associated analysis method were selected as support points:

Isotop	Emission line [keV]	Transition probability [%]	Analyse method
Pb-212	239	43,5	PSV
Ac-228	338	11,3	Trapez
Tl-208	583	30,6	Doublet with 511 keV Line Tl-208

Ac-228	911	26,6	Doublet with 965 keV Line Ac-228
Tl-208	2614	35,8	Trapez

The statistical uncertainty (95% confidence interval) of the count rates determined from the calibration spectrum for the above lines was between two and three percent. The figure below shows the customization using the appropriate wizard in Lab-Scout Works.



Nuclide	Energy [keV	Activity[Bq/k	Counts
Ac228	338	108	59673,9
Ac228	911	108	46682,7
Tl208	583	108	84221,5
Tl208	2614	108	19085,6
Pb212	239	108	369162

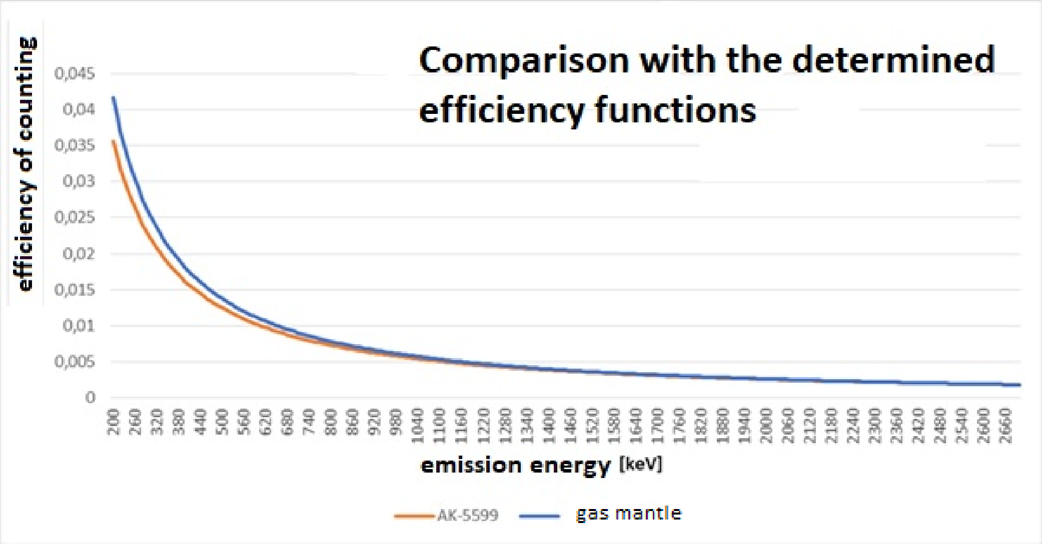
A 15,224700 B -1,143290 Ecut 150,000000 m 0,000300 Cursor 2521 keV; 0,0020 cps/(Bq/kg

The graphic shows the relative deviations of the measured support points from the determined efficiency function. Applying the efficiency function to the calibration spectrum results in the activity values summarized in the table below for the respective emission lines.

Isotop	Emission line [keV]	Nominal activity of the reference sample according certificate [Bq/kg]	With adapted efficiency calibration determined activity [Bq/kg]
Pb-212	239	108	113,8
Ac-228	338	108	105,3
Tl-208	583	108	102,3
Ac-228	911	108	108,7
Tl-208	2614	108	110,2

To verify the efficiency calibration, a potassium permanganate (KMnO4) sample was analyzed in the NQ7013 cup. The specific activity (percentage of the isotope K-40 in natural potassium) of KMnO4 is 7810 Bq/kg. The measurement showed an activity of 7579 Bq/kg. This corresponds to a deviation of only about 3%. Reasons for the deviation can be deviations of the fitted efficiency curve from the actual detector efficiency at this energy, the counting statistics, slightly different measurement geometry, different self-absorption (sample density) or contamination of the sample. However, the deviation of the measurement is well below the activity uncertainty of 10% specified for the reference sample.

A correction of the efficiency calibration with regard to the sample density is not necessary, since the lines to be examined have relatively high emission energies, the density itself and the density differences between the reference sample and ash samples are small. With a Th-232 point source (mantle) an efficiency curve was determined with practically no photon absorption analogous to the reference sample and adjusted to the reference point at 2614 keV (Fig. below). For the geometry of the sample container and the density values of the samples, a maximum absolute attenuation of less than 1% can be expected at this energy, so that the attenuation of the reference sample can be evaluated based on the deviation of both curves towards lower energies. The deviation at 660 keV (analyzed emission line with the lowest energy in the ash sample) is 8%. For the ash samples with a density in the range of 0.75 to 0.9 g/cm³, an additional attenuation of less than 3% can be assumed compared to the reference sample (1.0 g/cm³).



For a plausibility check, an efficiency curve was determined with a sample of the same geometry and nuclide composition (SN: AK-5600), but with a density of 1.6 g/cm³. The maximum deviation was about -7.5% at an energy of 660 keV.

Measurement campaign

For each sample, 15 measurements with a measurement time of one hour and three measurements with a measurement time of 12 hours were carried out. The samples were measured over a period of approx. one month, so that analyzes for the entire period are available for each sample. In order to exclude activity contributions from the ambient radiation, a background measurement was carried out at the beginning of the measurement campaign. The calibrations (energy/peak width and efficiency) also made at the beginning of the campaign were used for all analyses. In all analyses, the background spectrum was subtracted using the Lab-Scout Works software.

A nuclide list with the following emission lines was used for the analysis of the ash samples:

Isotop	Emission-Energy [keV]	Transition probability [%]
Cs-137	662	85
Bi-214	609	45,5
Bi-214	1764 + 1730	15,3 + 2,8 = 18,1
K-40	1461	10,55
Tl-208	2614	35,8

*) for Tl-208 the transition probability of the decay branch related to the parent nuclide Bi-212 was used, because the efficiency calibration was determined using the Th-232 activity of the reference sample.

At the end of the measurement campaign, another background measurement was carried out in order to register any changes. The table below shows the equivalent background contributions for the emission lines used to analyze the ash samples. The uncertainties given relate exclusively to the counting statistics. No significant change in the background was found.

Isotop	Emission-Energy [keV]	Measurement 26. 11. 2021	U (k=2) [%]	Measurement 29. 12. 2021	U (k=2) [%]
K-40	1461	921	3	908	3
Bi-214	1764	44	22	49	24
Tl-208	2614	50	9	56	11

Following the analysis of the ash samples, the wood pellet samples were examined. Due to the low level of activity, measurements were taken with measurement times of 12 hours to four days.

Measurement results

Ash samples

The results of the measurement campaign are summarized in the following tables. The results with a measurement time of one hour were not presented, since they lead to identical values in the context of the counting statistics. This will be discussed in more detail in the next section. The right column of the tables contains the statistical uncertainty for the number of pulses of the respective emission line determined during the measurement. This is purely informative and must not be equated with the measurement uncertainty. The actual measurement uncertainty to be specified is derived in the "Measurement uncertainty and traceability to a standard" section.

Sample 1

	Laboratory		Measurement 1	Measurement 2	Measurement 3	U (k=2) [%]
Date			2. 12. 2021	7. 12. 2021	14. 12. 2021	
Weight [kg]	0,86		0,86	0,86	0,86	
Cs-137	490 ± 38		607	604	603	1
K-40	1558 ± 116		2170	2223	2188	1
Ra-226	44 ± 2,5	Bi-214	120	118	118	9
Ra-228	67 ± 3,4					
Th-228	72 ± 4	Tl-208	75	71	66	7

Sample 2

	Laboratory		Measurement 1	Measurement 2	Measurement 3	U (k=2) [%]
Date			1. 12. 2021	8. 12. 2021	15. 12. 2021	
Weight [kg]	0,76		0,76 (0,95)	0,76	0,76	
Cs-137	205 ± 17		225	219	216	2
K-40	1208 ± 105		1410	1468	1491	2
Ra-226	128 ± 6	Bi-214	114	119	114	9
Ra-228	84 ± 4,2					
Th-228	80 ± 5,3	Tl-208	79	78	77	7

Sample 3

	Laboratory		Measurement 1	Measurement 2	Measurement 3	U (k=2) [%]
Date			3. 12. 2021	9. 12. 2021	16. 12. 2021	
Weight [kg]	0,87		0,87	0,87	0,87	
Cs-137	275 ± 22		305	299	301	1
K-40	1621 ± 120		2038	2016	2009	2
Ra-226	75 ± 4,1	Bi-214	107	108	117	10
Ra-228	74 ± 3,8					
Th-228	68 ± 4,8	Tl-208	75	68	77	7

Sample 4

	Laboratory		Measurement 1	Measurement 2	Measurement 3	U (k=2) [%]
Date			6. 12. 2021	10. 12. 2021	17. 12. 2021	
Weight[kg]	0,87		0,87	0,88	0,88	
Cs-137	90 ± 7,4		101	101	100	2
K-40	1644 ± 159		2107	2119	2122	1
Ra-226	96 ± 4,9	Bi-214	120	134	131	9
Ra-228	76 ± 3,5					
Th-228	70 ± 4,4	Tl-208	75	77	77	6

Sample 5

	Laboratory		Measurement 1	Measurement 2	Measurement 3	U (k=2) [%]
Date			30. 11. 2021	13. 12. 2021	20. 12. 2021	
Weight [kg]	0,86		0,86	0,86	0,86	
Cs-137	79 ± 6,4		83	80	82	3
K-40	2046 ± 174		2520	2499	2518	1
Ra-226	77 ± 4,4	Bi-214	176	181	159	7
Ra-228	94 ± 3,4					
Th-228	90 ± 5,1	Tl-208	90	84	81	6

Wood pellets

As expected, the activity of sample 7 (0.7 Bq/kg) could not be detected with the Lab-Scout even after a measurement time of 12 to 24 hours. However, for sample 6 (6.9 Bq/kg), the device provided reproducible readings. With such low activities, a significant influence of the background measurement is to be expected. For this reason, the analysis results were determined using three different 12-hour background measurements. Two of the background measurements were taken shortly before and after the measurement of the wood pellet samples. The third background measurement took place more than a month before the wood pellet measurement. The local dose rate at the measuring point was approx. 110 nSv/h.

		activity concentration in Bq/kg with background measurement from		
Measurement	time	26. 11. 2021	29. 12. 2021	13. 1. 2022
7. 1. 2022	24 h	5,2	6,1	6,6
11. 1. 2022	4 d	3,1	4,9	4,9
18. 1. 2023	12 h	4,7	5,9	6,6

19. 1. 2022	12 h	-	4,3	4,0
20. 1. 2022	12 h	3,9	6,0	6,6
Average		4,22	5,44	5,74

An exact statistical analysis of the distribution of the measured values was not carried out due to the small number of data and different measuring times. The results using the two timely background measurements from December 29, 2021 and January 13, 2022 agree well, while using the background measurement from November 26, 2021 leads to an underestimation of the activity.

Reproducibility of the measured values and statistical uncertainty

To investigate the reproducibility of the results, the mean value and the standard deviation were determined for the 15 1-hour measurements of the samples. The standard deviation can be compared to the uncertainty given by Lab-Scout Works from the respective counting statistic. The table below shows the values for the analysis of the Cs-137 peak.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Average from 3 measurements Each 12h [Bq/kg]	605	220	302	101	82
Average from 15 measurements each 1 h [Bq/kg]	604	220	305	101	80
Standard deviation from 15 measurements each 1 h [%]	1,23	2,28	2,66	4,80	6,39
For sample typical standard uncertainty with 1 h measuring time [%]	1,5	2,5	2	4,5	5
Lowest 1-h value [Bq/kg]	590	211	289	90	72
Biggest 1-h value [Bq/kg]	617	230	323	108	89

Measurement uncertainty and traceability to a standard

Causes of the measurement uncertainty

The activity is determined using the following formula:

$$A = \frac{N}{T \cdot P \cdot \mathrm{m} \cdot \eta}$$

A: Weight-specific activity of an isotope

N: Number of registered decays in the peak of the emission line used for the analysis (peak area)

T: measurement time

P: Transition probability of the emission line used for the analysis

m: mass of the sample

η: Counting efficiency of the detector for the emission energy of the emission line used

The uncertainties for the measurement time and the transition probability are negligible compared to the other variables and are not considered further. The uncertainty of the mass determination is set at 2% based on the data sheet, the resolution of the display and the factory calibration. The main factors in the uncertainty balance are the determined peak area and above all the counting efficiency of the detector.

The statistical uncertainty of the peak area is estimated for each emission line using the count statistic according to the analysis method used. Systematic deviations due to possibly existing non-linearities of the background in the energy range of the emission line cannot be reliably assessed. The statistical uncertainty is calculated and reported by the software.

The traceability of the measurement is guaranteed by determining the detector efficiency using a reference sample and adjusting the energy-dependent efficiency curve. The uncertainty of the counting efficiency is determined by several factors:

- Uncertainty of the reference activity stated in the certificate (5% for AK-5599)

- Adaptation of the efficiency curve due to statistical uncertainties when determining the support points (peak area)

- Physically caused, systematic deviations of the model function of the efficiency curve from the real detector properties at the point of the respective emission line

The analytical assessment of the statistical uncertainties of the efficiency curve at the positions of the emission lines to be analyzed using the reference points is complex, so that an assessment based on 20 measurements with an identical reference was carried out. The cause of the uncertainty is the statistical uncertainty of the peak areas determined during the measurement at the support points.

The two shape parameters of the fitting function were determined for each of the 20 measurements. For each of the 20 functions obtained, the efficiency at the positions of the emission lines to be analyzed later (662 keV, 1461 keV, 1764 and 2614 keV) was calculated. A check of the distribution of these 20 values resulted in a uniform distribution. The relative standard deviation of the efficiency for an emission line can be determined from the quotient of the standard deviation and the expected value of the 20 equally distributed individual values.

In order to limit the time required, the measurements were not carried out with the reference sample AK-5599, but with a thorium mantle. The measurement time (1 hour) was adjusted in such a way that the statistical error of the peak areas for the sample AK-5599 and the mantle correspond (2%). Both samples provide a very good match of the function curve and the same systematic deviations of the fitted curve at the support points. This allows for comparability. The table below shows the results of the estimation.

	Cs-137 662 keV	K-40 1461 keV	Bi-214 1764 keV	Tl-208 2614 keV
Relative Standard-uncertainty of the detector-efficiency calibration for the considered emission lines	0,67%	0,5%	0,65%	0,94%

The uncertainties are all almost an order of magnitude below the uncertainty of the activity of the reference sample and are relatively close together so that using a generally accepted uncertainty value of 1% is acceptable.

The systematic deviation of the model function cannot be determined because the number of support points is limited. The maximum deviation D of 5% occurring at one of the reference points should be used as a measure here. This deviation cannot be regarded as a normally distributed random variable and must therefore be added in full.

Measurement uncertainty balance

The following applies to the uncertainty of the efficiency at the position of the emission line i in the spectrum:

$$\eta_i = \frac{N_i}{T \cdot P_i \cdot \mathrm{m} \cdot \mathrm{A}_i}$$

ηi: Detector efficiency at position of emission line i in the spectrum

Ni: with an adapted efficiency curve to be assumed peak area of the emission line i

The measurement time T and the transition probability are not considered as influencing variables, since their uncertainty is at least one order of magnitude below that of the mass (m), activity (Ai) and peak area (Ni) variables. This results in the following relationship for the relative uncertainty of η:

$$\frac{u(\eta)}{\eta} = \sqrt{\left(\frac{u(N_i)}{N_i}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(A_i)}{A_i}\right)^2}$$

The terms within the root describe the relative variances of the individual influencing variables. According to the certificate of the reference sample, the relative standard uncertainty of the activity is 0.05, that of the mass determination is 0.02 and the experimentally determined (see above) relative standard uncertainty of the peak area is 0.01.

The relative uncertainty for the detector efficiency is therefore:

$$\frac{u(\eta)}{\eta} = \sqrt{0{,}01^2 + 0{,}02^2 + 0{,}05^2} \approx 0{,}055$$

Accordingly, the relative uncertainty of the activity determination using the previously determined uncertainty of the detector efficiency is:

$$\frac{u(A_i)}{A_i} = \sqrt{\left(\frac{u(N_i)}{N_i}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(\eta_i)}{\eta_i}\right)^2}$$

The relative uncertainty of the peak area is taken from the results of the respective measurement. The following table shows an example of the relative uncertainties for the peak areas (typical value from measurements) and activities (using the formula above) of Cs-137 for a measurement time of one and twelve hours, respectively. The value 0.02 is also used here for the uncertainty of the mass determination.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
$u^*_{rel}(N_{Cs\text{-}137})$ bei T = 1h	0,015	0,025	0,02	0,045	0,05
$u^*_{rel}(N_{Cs\text{-}137})$ bei T = 12h	0,005	0,01	0,005	0,01	0,015
$u^*_{rel}(A_{Cs\text{-}137})$ bei T = 1h	0,061	0,064	0,062	0,074	0,077
$u^*_{rel}(A_{Cs\text{-}137})$ bei T = 12h	0,059	0,06	0,059	0,06	0,061

A confidence interval of 95% (k = 2) should be used to indicate the uncertainty. The maximum expected systematic deviation of the actual detector efficiency from the characteristic curve (D = 0.05) must be added to this value:

$$U(A_{Cs-137}) = A_{Cs-137} \cdot (2 \cdot u^*_{rel}(A_{Cs-137}) + D)$$

The following table shows the absolute uncertainties to be expected for the five samples

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
A_{Cs-137} [Bq/kg]	605	220	302	101	81
$U(A_{Cs-137})$ bei T = 1h [Bq/kg]	104	39	53	20	17
$U(A_{Cs-137})$ bei T = 12h [Bq/kg]	102	38	51	17	14

Conclusions

The main factors influencing the measurement uncertainty are the uncertainty of the activity of the reference sample and the assumed systematic deviation of the actual detector efficiency from the fitted function at the positions of the emission lines. As expected, the uncertainties in determining the mass and adapting the function using support points play a subordinate role. The influence of the measurement time on the counting statistics only becomes clearly visible for activities in the range below 100 Bq/kg.

In order to reduce the uncertainty, reference samples with a lower uncertainty of the specified activity would therefore have to be used. The systematic deviation of the efficiency function can be reduced by using reference samples that already contain the emission lines to be analyzed later.

Evaluation of the measurement results and the measurement method

The results of all measurements including the error limits are consistent and reproducible. The derivation of the measurement uncertainty can be presented plausibly. The measured Cs-137 and Tl-228 activities of all samples show a very good agreement with the results of the laboratory analysis. The measurement results tend to be in the range of approx. 5% to 10% above those of the laboratory values. This should be an indication of a systematic deviation due to the efficiency calibration of both measuring devices. Sample 1 shows a significantly higher deviation of almost 25% for Cs-137. Nevertheless, the confidence intervals of both analyzes overlap (upper limit laboratory = 528 Bq/kg; lower limit measurement = 501 Bq/kg). Under the assumption of the above-mentioned systematic overestimation due to the efficiency calibration, the deviation is put into perspective.

The measured K-40 activities are about 25% above the values from the laboratory analyses. Here, too, only sample 1 shows a higher deviation from the laboratory value at 40%. This deviation is not plausible because the determination of the potassium permanganate sample with practically defined activity resulted in a deviation of minus 5 percent. With an equivalent of about 900 Bq/kg, the contribution of the ambient radiation is already in the range of the sample activities. Therefore, the measurement results were determined again without deducting the background spectrum and the contribution of the background measurement was deducted. There were only minor deviations in the counting statistics. Furthermore, the results were calculated using the second background measurement (taken place after the end of the measurement campaign). The deviations are in the single-digit Bq/kg range.

To evaluate the above deviations, samples 1 to 5 and the reference standard (AK5599) were examined using HPGe analysis as part of an internship at the TU Dresden. An uncertainty analysis of the analysis method was not carried out. The intrinsic efficiency of the detector was extended by a geometry factor (Marinelli cup) using the reference standard measurement. This resulted in the following results:

Cs-137 activities in Bq/kg

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Laboratory	490	205	275	90	79
Lab Scout	605	220	302	101	82
TU Dresden	**550**	**200**	**279**	**97**	**80**

K-40 activities in Bq/kg

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Laboratory	1558	1208	1621	1641	2046
Lab Scout	2188	1461	2016	2119	2518
TU Dresden	**2184**	**1611**	**1975**	**2101**	**2470**

In the K-40 values of the measurements from the TU Dresden and the Lab Scout agree well. The results for sample 1 also match well, but here too there is a general slight overestimation of the Cs-137 values. This is probably due to the systematic deviation of the Lab Scout efficiency curve at 660 keV, since the same reference standard was used. Looking at the efficiency curve in the efficiency calibration section, there is a deviation of approx. -5.5% at 583 keV, while the interpolation in the range from 911 keV to 2614 keV shows a deviation of approx. +1% for K-40 (1463 keV) can be expected. A plausible explanation for the difference to the laboratory measurement could not be found due to a lack of further information about the laboratory measurement.

The measurement method delivers reliable measurement values for the sample type and the observed activity ranges even with measurement times of one hour. With the derived uncertainties in the range of 15 to 20 percent for the Cs-137 activity determination, the Lab-Scout with the Lab-Scout Works operating software meets the requirements of a fast method for the analysis of ash samples from biomass power plants. No calibration or maintenance work was necessary during the approximately one-month campaign. This shows that the measuring device can generally be operated with very little effort in terms of personnel and material.

Application limits result from the activity ratios of the isotopes Cs-137 and Bi-214 or Tl-208 as part of a doublet. Above a peak area ratio of 10:1, the uncertainty for the emission line with the smaller area increases sharply. For the analysis of cesium, this is the case when the sum of the activities of Bi-214 and Tl-208 exceeds twenty times the activity of Cs-137.

The detection limits of the Cs-137 analysis depend on the local dose rate at the measuring point and on the activities of the natural radionuclides contained in the sample. The measurements of the wood pellet sample 6 have shown that a reproducible Cs-137 measurement is possible at activity concentrations in the range of 5 to 10 Bq/kg with a measurement time of 12 hours. The standard deviation of the measurements can be assumed to be 15% to 20% based on the measurement data. The relative total measurement uncertainty (k = 2) is thus in the range of 40% to 50%. If one assumes that the activities of natural radionuclides in biomaterial are generally at a similar level, the analysis method also offers the possibility of identifying critical material before it is burned.