

BAM-U024

Adsorbed organically bound halogens (AOX) in soil

BAM-U025

Adsorbed organically bound halogens (AOX) in sludge

Certification Report

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1 Introduction

Adsorbed organically bound halogens (AOX) is a summation parameter that includes chlorine, bromine and iodine containing compounds that adsorb to charcoal and lead to the release of volatile hydrogen halogenides on combustion which are quantified as chlorine equivalent electrochemically. The procedure for determination of AOX in water is laid down in EN ISO 9562:2004 and in DIN 38414-18:2019 for the determination in sludges and sediments [1,2]. The latter is often also applied to soil.

The analytical procedure includes adsorption of organohalogen compounds to charcoal and removal of inorganic water soluble halogenides from the sample. After combustion of the sample and the charcoal in an oxygen stream and purification with concentrated sulfuric acid the volatile hydrogen halogenides (chloride, bromide, iodide) are quantified argentometrically using microcoulometry.

BAM-U024 and BAM-U025 replace former soil reference materials ERM-CC010, ERM-CC011 and ERM-CC012. The certification followed the rules laid down in ISO 17034 [3] and ISO Guides 31 and 35 [4, 5].

2 Candidate materials

2.1 Preparation of the candidate materials

The carbon-rich soil starting material for BAM-U024 was obtained from a contaminated site in Wittstock, Germany. After air-drying and classification by means of a sieving station the particle size fraction $< 63 \mu\text{m}$ (4.60 kg) was homogenised using drum hoop mixer (J. Engelsmann AG, Ludwigshafen, Germany) for 12 h and bottled in 10 mL amber glass bottles using a Retsch spinning riffler with 8 tubes for back-maxing ("cross-riffling") and 10 tubes for a procedure of portioning. 800 bottles containing (5.7 ± 0.1) g each were sealed with screw caps equipped with Teflon inserts and stored at $-20 \text{ }^\circ\text{C}$.

The candidate material for BAM-U025 was a sewage sludge with a water content of about 70% was obtained from a sewage treatment plant near Berlin, Germany, and freeze dried. The material was sterilised by Co-60 irradiation at Hahn-Meitner-Institute, Berlin, Germany. After grinding with a Retsch centrifugal mill the material was classified by sieving. The fraction $< 100 \mu\text{m}$ (3.53 kg) was homogenised in the drum hoop mixer for 12 h and subsequently 655 amber glass bottles (10 mL) with screw caps equipped with Teflon inserts were filled manually with (5.4 ± 0.2) g of the material.

2.2 Characterisation of the matrix

Table 1 comprises the chemical characterisation of the matrix of the candidate material. The water contents are at equilibrium with the atmosphere under typical laboratory conditions and correspond to the relatively high contents of organic carbon in both materials.

Table 1: Matrix characterisation of BAM-U024 and BAM-U025

Parameter	Method	BAM-U024	BAM-U025
Particle size range (μm)	Sieving	< 63	< 100
Water content (%)	Drying loss at $105 \text{ }^\circ\text{C}$	4.3 ± 0.2	14.2 ± 0.1
CHN-content (%)	Combustion	C: 21.2 ± 0.6 H: 2.3 ± 0.1 N: 0.41 ± 0.01	C: 28.8 ± 0.8 H: 5.6 ± 0.1 N: 4.8 ± 0.1

2.3 Minimum sample intake

The minimum sample intake for one determination is technically restricted by the method laid down in DIN 38414-18:2019. The adsorption/filtration step does not allow more than 100 mg of the material to be treated per analysis. Depending on composition and density of the matrix this may be as small as 50 mg which is also the typical intake used in routine analytical practise. Hence, this intake was used for the homogeneity study and the certification intercomparison.

3 Homogeneity study

Twenty units were selected in case of both materials equidistantly from the order of bottling of the whole batch. They were analysed three times each according to DIN 38414-18:2019 using a sample intake of 50 mg. The whole set of 60 samples was extracted once on each of three consecutive days. Means and standard deviations are summarised in Figures 1 and 2. For the measurement data and the analysis of variance see the ANNEX. No evidence suggesting a rejection of the hypothesis that both materials are sufficiently homogeneous was observed. The means of the homogeneity study were 44.16 mg/kg (BAM-U024) and 248.061 mg/kg (BAM-U025). The uncertainties of the AOX contents between the bottles u_{bb} were estimated at 0.6734 mg/kg (BAM-U024) and at 3.611 mg/kg (BAM-U025) or expressed in relative terms as $u_{bb,r}$ as 0.01523 (BAM-U024) and as 0.0146 (BAM-U025).

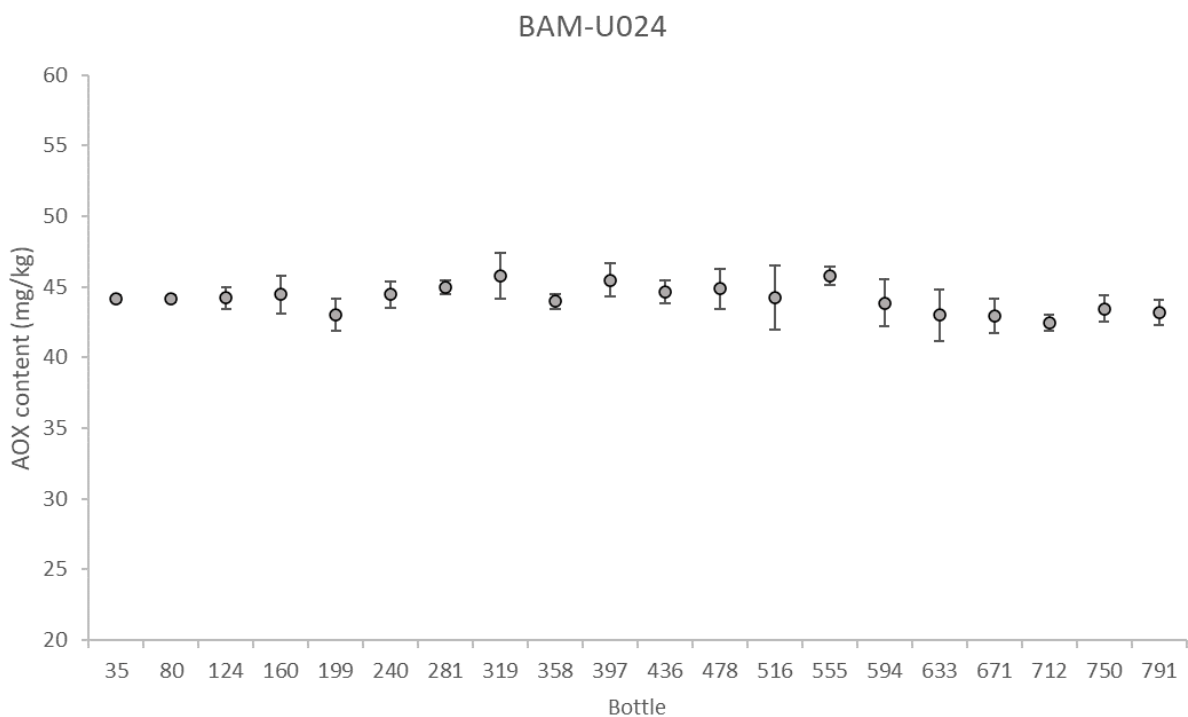


Fig. 1: Homogeneity study of the AOX content on selected bottles of BAM-U024 (means and standard deviations $n = 3$).

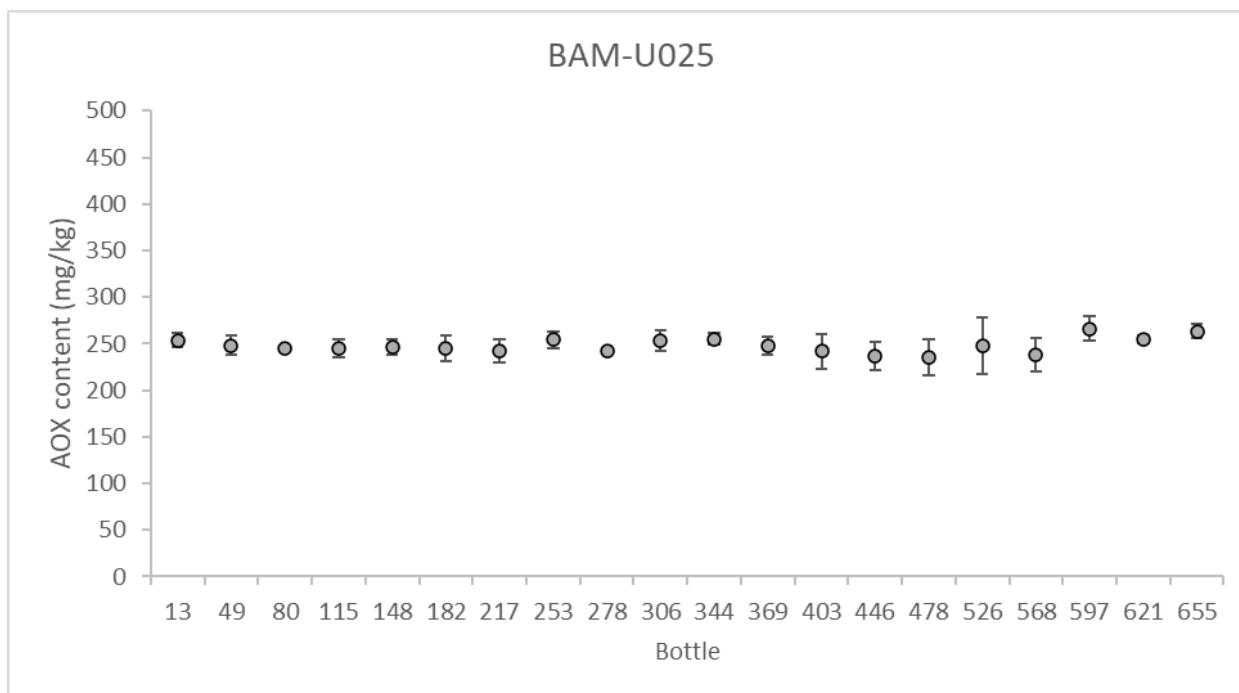


Fig. 2: Homogeneity study of the AOX content on selected bottles of BAM-U025 (means and standard deviations n = 3).

4 Stability study

From earlier experience with organics [6] in various matrices a temperature-driven deterioration of the AOX content was to be expected for this material. Selected units of the candidate materials were submitted to a so-called isochronous [7] accelerated ageing at temperatures between +4 and +60 °C over periods up to 12 months as shown in Table 2. Reference samples were stored at – 80 °C directly after bottling. After experience with former AOX matrix materials (ERM-CC010, ERM-CC011, ERM-CC012 [8]) and organic analytes in other soil or sludge matrices having been stored over years at ambient temperatures hardly any deterioration of the AOX content was expected for exposure periods up to six months. Therefore, units exposed between +4 °C and +60 °C up to 12 months and thereafter stored at -20 °C were selected to assess AOX content stability. Selected units including the reference units (– 80 °C) were analysed for the AOX content using the DIN standard method under repeatability conditions. These analyses were awarded as a contract to one of the interlaboratory comparison participants. For the individual measurement data see the ANNEX.

Table 2: Accelerated ageing of selected units of BAM-U024 and BAM-U025: exposition temperatures, periods and number of exposed units.

Ageing time (months)	+4 °C	+22 °C	+40 °C	+60 °C	Remark
3	-	-	x	-	<i>initial study</i>
6	-	-	x	x	<i>initial study</i>
12	x	x	x	x	<i>initial study</i>
24	x	x	-	-	<i>post certification monitoring</i>
36	x	x	-	-	<i>post certification monitoring</i>

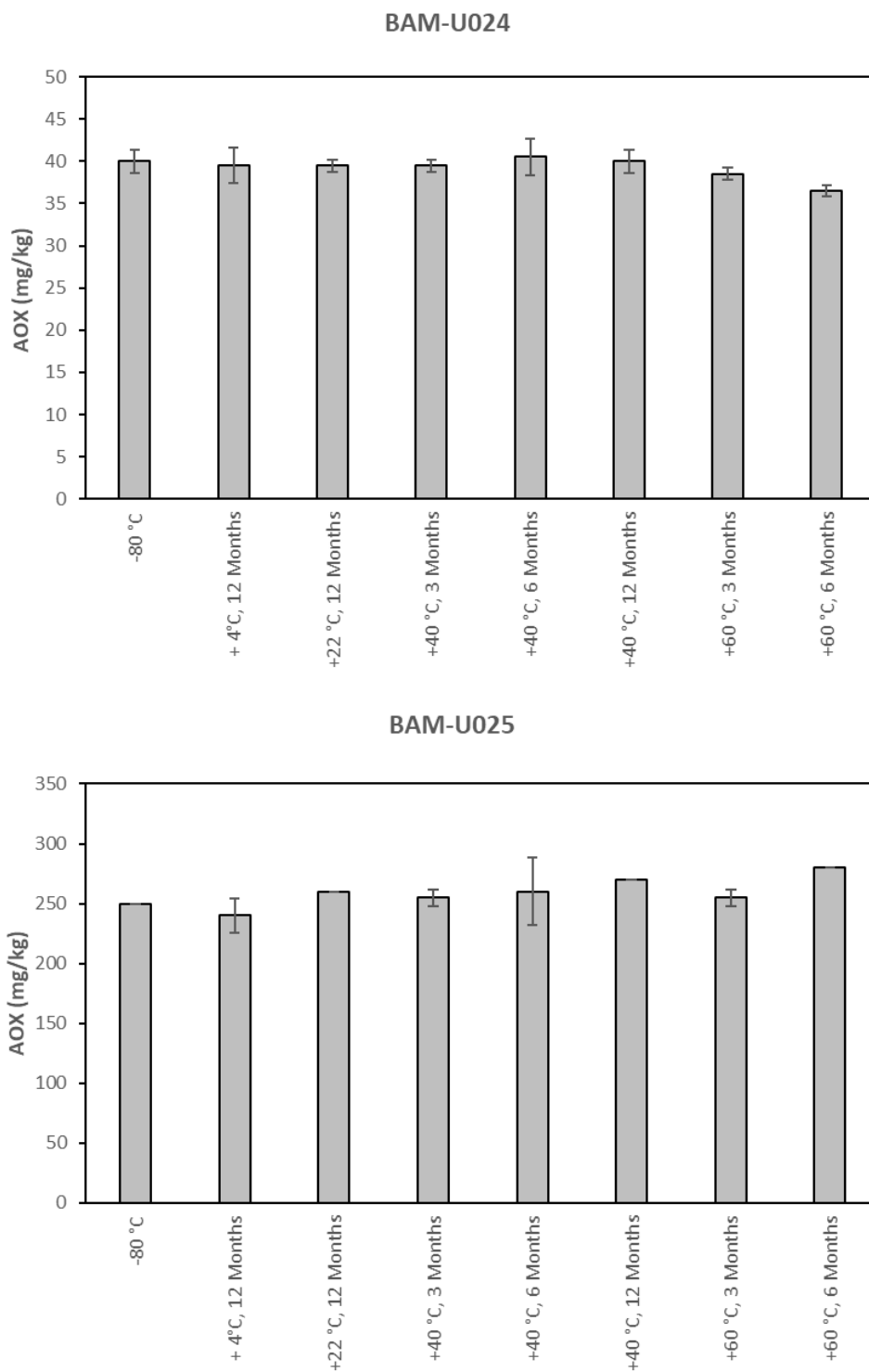


Fig. 3: Development of the AOX content in BAM-U024 and BAM-U025 after accelerated ageing (means and standard deviations n = 2).

Based on previous experience with AOX in the reference materials ERM-CC011, ERM-CC012, ERM-CC013 and other matrix materials used for proficiency testing it can be stated as expert judgement that the AOX content at storage temperature

of -20 °C is stable indefinitely. The reference temperature (-80 °C) was chosen to support this information over the period of availability of the CRMs. Similar to earlier soil reference materials (ERM-CC011, ERM-CC012, ERM-CC013) the AOX content did not display any significant decrease after accelerated ageing at ambient temperature and even at 40 °C and 60 °C within six months (Fig. 3). Therefore, the reference materials are considered stable at the storage temperature (-20 °C) and any estimation of a significant degradation based on a temperature driven model [6] was not applicable. Although the shelf life at the storage temperature of -20 °C appears practically indefinite, any prolonged exposure to ambient and especially higher temperatures may nevertheless reduce the time of validity of the certified values. The transportation/delivery time should be kept at the possible minimum and any exposure to elevated temperatures should be avoided. A post-certification monitoring will be scheduled with units stored at -80 °C, -20 °C, 4 °C and 20 °C within five years after certification.

5 Certification study

5.1 Selection of participating laboratories

A total of ten laboratories were invited to participate in the certification exercise on grounds of their satisfactory performance in a recent proficiency testing round on AOX analysis in soil operated by BAM in 2020. Selection criteria included in addition to trueness of results also the consistency of documentation of the analytical procedure according to DIN 38414-18:2019 and the declaration of commitment to comply with these requirements during the certification analyses. Additionally, the BAM laboratory responsible for candidate material production and homogeneity measurements took part in this exercise. The participants are listed in alphabetical order of the locations in Table 3 (not identical with the numbering of the results in Table 4).

Table 3: Participants involved in the certification exercise in alphabetical order of location

M & S Umweltprojekt GmbH	Bad Muskau, Germany
BIOLAB Umweltanalysen GmbH	Braunschweig, Germany
Berghof Analytik + Umweltengineering GmbH	Chemnitz, Germany
GEO-data GmbH	Garbsen, Germany
PETROLAB GmbH	Glaubitz, Germany
ICA - Institut für Chemische Analytik GmbH	Leipzig, Germany
CLG Chemisches Labor Dr. Graser KG	Schonungen, Germany
GBA Analytical Services GmbH	Vaterstetten, Germany

Six replicate AOX determinations using an intake of 50 mg of the respective candidate material were to be performed by each laboratory. A questionnaire on the laboratory procedures had to be filled in. Results returned to BAM were scrutinised for consistency.

5.2 Interlaboratory comparison (ILC) results and certified values

The results of the certification study are collected in Table 4 and Fig. 4 (p. 10) were evaluated in accordance with ISO Guide 35 [5]. The method detailed in the

DIN standard leaves little liberty for procedural variants and consequently the scrutiny of laboratory protocols did not reveal any association of results and laboratory settings.

Table 4: Data sets received from the participants in the certification study of BAM-U024 and BAM-U025 in mg/kg

BAM-U024	Replicate							
	# 1	# 2	# 3	# 4	# 5	# 6	mean	SD ^a
C01	56.65	61.69	63.89	60.71	35.89	46.56	54.3	10.88
C02	45.93	41.46	44.95	44.35	43.1	44	43.97	1.55
C03	44.37	44.72	40.7	39.53	39.74	40.85	41.65	2.30
C04	38.2	39.7	39.7	40.2	38	37.9	38.95	1.03
C05	33.6	25.3	27.8	23.3	23.9	24.7	26.43	3.84
C06	43.314	39.046	39.634	44.547	41.934	41.127	41.60	2.11
C07	42.2	44.2	42.1	43.7	40.6	43.1	42.65	1.30
C08	43.25	47.45	44.73	46.63	49.2	42.97	45.71	2.47
C09	42.11	42.04	42.89	41.6	42.97	42.75	42.39	0.56
C10	41.1	39.3	42.3	42.2	41.1	40.1	41.02	1.17

^a standard deviation

BAM-U025	Replicate							
	# 1	# 2	# 3	# 4	# 5	# 6	mean	SD ^a
C01	218.6	207.6	202.9	221.7	225.6	213.6	215.00	8.64
C02	310	318.3	327	309	328.5	339	321.97	11.69
C03	-	-	-	-	-	-	-	-
C04	244	260	261	262	246	248	253.50	8.34
C05	267.1	252.1	250.8	253	262.9	259.6	257.58	6.63
C06	259.7	268.09	256.71	281.68	256.43	254.1	262.79	10.46
C07	230	232	251	241	228	230	235.33	8.94
C08	276.6	274.8	254.5	250.3	246.9	274.7	262.97	13.81
C09	243.8	246.8	242.7	244	243.9	246.9	244.68	1.74
C10	253	259	249	258	254	259	255.33	4.03

^a standard deviation

Although all participants in the intercomparison followed the same standardised procedure, significant differences caused by different implementations in different laboratories were to be expected. Thus, there was no good reason for assuming that the single values measured by the different laboratories would belong to a common mother distribution. This was confirmed by the statistical analysis within which the following statistical parameters were calculated using the software SoftCRM [9, 10].

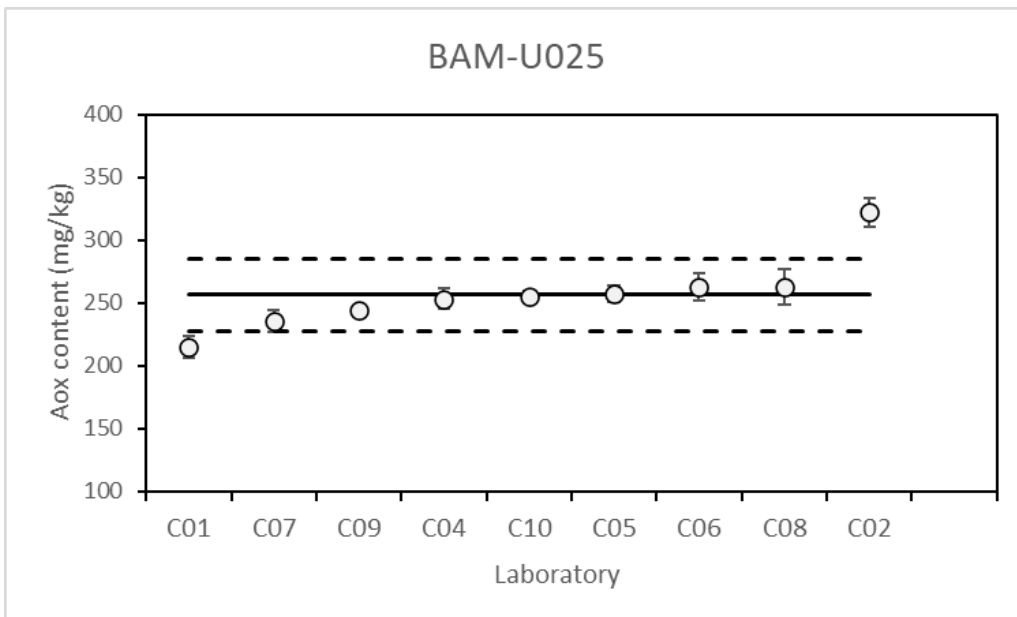
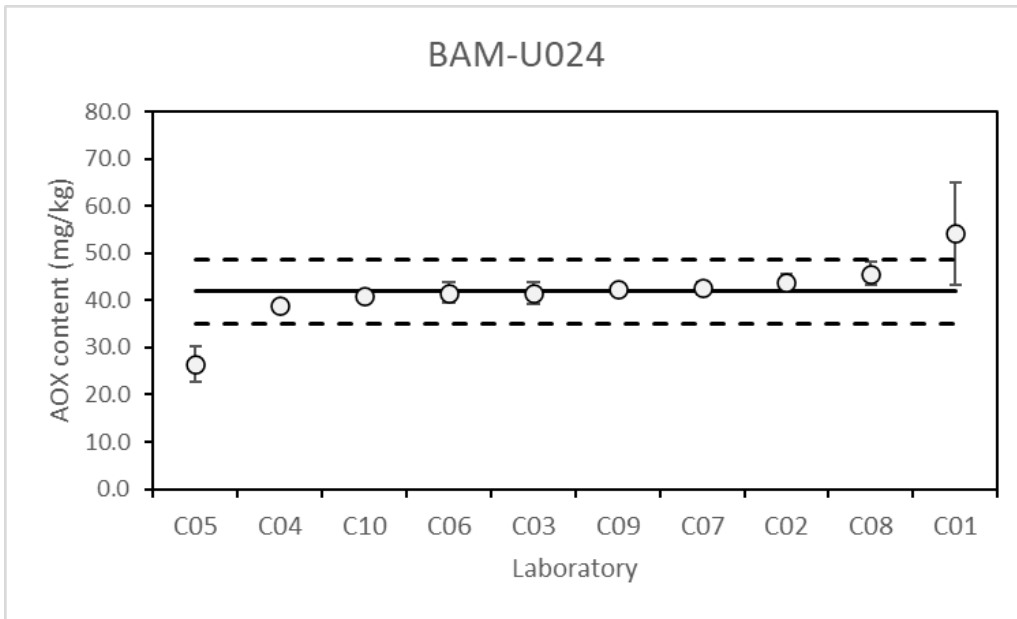


Fig. 4: Interlaboratory comparison results (data from Table 4); laboratory means and standard deviation, total means and standard deviations before outlier elimination.

The following statistical tests were carried out (at significance levels α of 0.05 and 0.01):

- Cochran test for the identification of outliers with respect to laboratory variance
- Grubbs test for the identification of outliers with respect to the mean
- Dixon and Nalimov tests for the verification of possible outlier indications
- Kolmogorov-Smirnov test (Lilliefors version) for the normality test
- Tests for variance homogeneity, skewness and kurtosis

The main features in case of BAM-U024 are as follows:

- Scheffé test: Many laboratory data sets differ significantly if compared directly.
- Snedecor F test: Differences between laboratories are statistically significant ($\alpha = 0.01$).
- Bartlett test: Variances are not homogeneous ($\alpha = 0.01$).
- Cochran test: C01 and C05 are outliers ($\alpha = 0.01$).
- Dixon test: C05 is an outlier ($\alpha = 0.01$), C01 is a straggler ($\alpha = 0.05$).
- Nalimov test: C01 and C05 are stragglers ($\alpha = 0.05$).
- Grubbs test: C05 is a straggler ($\alpha = 0.05$).
- Kolmogorov-Smirnov-Lilliefors test: Laboratory means are normally distributed ($\alpha = 0.05$).
- Skewness & kurtosis test: Laboratory means are not normally distributed ($\alpha = 0.05$).

The main features in case of BAM-U025 are as follows:

- Scheffé test: Many laboratory data sets differ significantly if compared directly.
- Snedecor F test: Differences between laboratories are statistically significant ($\alpha = 0.01$).
- Bartlett test: Variances are not homogeneous ($\alpha = 0.05$).
- Cochran test: No outliers detected.
- Dixon test: C02 is an outlier ($\alpha = 0.01$).
- Nalimov test: C02 is an outlier ($\alpha = 0.01$).
- Grubbs test: C02 is a straggler ($\alpha = 0.05$).
- Kolmogorov-Smirnov-Lilliefors test: Laboratory means are not normally distributed ($\alpha = 0.05$).
- Skewness & kurtosis test: Laboratory means are not normally distributed ($\alpha = 0.05$).

The values of laboratories C01 and C05 were removed in case of BAM-U024 and the values of laboratories C01 and C02 in case of BAM-U025 prior to evaluation of the certified values. The values of laboratory C01 were regarded as unreliable (highest values in BAM-U024, lowest values in BAM-U025) and therefore removed also in case of BAM-U025. The certified values are the ILC means w_{cert} after outlier removal and the expanded uncertainties U are derived from the ILC standard deviations s as outlined in Table 5.

Table 5: Evaluation of the certified AOX contents of BAM-U024 and BAM-U025 based on the mean w_{cert} and standard deviation s of the interlaboratory comparison after removal of the respective outliers (n = number of accepted data sets).

		After outlier removal		
	Unit	BAM-U024	BAM-U025	
w_{cert}	mg/kg	42.24	253.17	= ILC mean
s	mg/kg	2.0089	10.0238	
u_{char}	mg/kg	0.7102	3.7886	= $s/n^{1/2}$
$u_{\text{char,r}}$	-	0.01681	0.01400	= $u_{\text{char}}/w_{\text{cert}}$
$u_{\text{bb,r}}$	-	0.01540	0.01455	see 3./A.2
$u_{\text{com,r}}$	-	0.02280	0.02019	= $(u_{\text{char,r}}^2 + u_{\text{bb,r}}^2)^{1/2}$
u_{com}	mg/kg	0.9632	5.2847	= $w_{\text{cert}} \cdot u_{\text{com,r}}$
U	mg/kg	1.9264	10.2243	= $2 \cdot u_{\text{com}}$

After rounding according to DIN 1333 [11].

<i>Value</i>	mg/kg	42	253	
U	mg/kg	2	11	

5.3 Traceability

The AOX content is defined by the method employed for its determination as laid down in DIN 38414-18:2019. The certified values of BAM-U024 and BAM-U025 each represent the combined mass fraction of volatile halogenides as determined according to DIN 38414-18:2019.

6 Information on the proper use of BAM-U024 and BAM-U025

6.1 Shelf life

From the stability study no reasonable shelf life at -20 °C could be estimated as no decrease of the AOX content could be detected at temperatures up to 40 °C. A very conservative estimate for the stability is six years from the date of certification. The validity of this estimate will be maintained by post-certification stability monitoring five years after certification. Therefore, the certificate will be valid until then for at least 24 months beginning with the dispatch of the material from BAM.

6.2 Transport, storage and use

The stability of the content of AOX allows dispatching the material at ambient temperature. On receiving, it is to be stored at -20 °C. Before withdrawing a subsample the bottle must have reached ambient temperature. Thereafter, the bottle must be closed tightly and stored at -20 °C again. The water content remains stable when the material is treated as described.

6.3 Safety instructions

BAM-U024 was not sterilised, however, it is supposed to not exhibit any biological activity due to having been air-dried to constant mass and displaying a water content of 4.3%. No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of moderately contaminated

environmental matrices. Any unintended contact to this material should be treated as the contact to a dry soil without specifically hazardous properties.

BAM-U025 was sterilised using Co-60 irradiation designed for this purpose prior to processing and is supposed to not exhibit any biological activity due to having been air-dried to constant mass and displaying a water content of 14.2%. No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of moderately contaminated environmental matrices. Any unintended contact to this material should be treated as the contact to a dry sludge without specifically hazardous properties.

It is strongly recommended to handle and dispose of the reference material in accordance with the guidelines for hazardous materials legally in force at the site of end use and disposal.

6.4 Legal notice

Neither the Bundesanstalt für Materialforschung und -prüfung (BAM) nor any person acting on their behalf make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document may not infringe privately owned rights, or assume any liability with respect to the use of, or damages resulting from the use of any information, material, apparatus, method or process disclosed in this document.

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ANNEX: Homogeneity and stability, measurement data

Results of the homogeneity study on BAM-U024. SD – Standard deviation.

Bottle No.	Replicate			Mean (mg/kg)	SD (mg/kg)
	1 (mg/kg)	2 (mg/kg)	3 (mg/kg)		
35	44.19	43.89	44.36	44.14	0.24
80	44.19	43.89	44.36	44.14	0.24
124	43.74	45.08	43.82	44.21	0.75
160	44.76	45.65	42.98	44.46	1.36
199	44.07	43.17	41.77	43.01	1.16
240	43.60	44.36	45.45	44.47	0.93
281	45.24	45.22	44.43	44.96	0.46
319	46.81	43.94	46.58	45.77	1.59
358	44.40	43.36	44.12	43.96	0.53
397	45.28	46.72	44.41	45.47	1.17
436	44.69	45.41	43.81	44.64	0.80
478	45.98	43.20	45.74	44.87	1.40
516	46.85	42.58	43.29	44.24	2.29
555	45.46	45.29	46.50	45.75	0.65
594	43.29	42.56	45.74	43.86	1.66
633	45.08	41.74	42.18	43.00	1.81
671	44.24	42.70	41.88	42.94	1.20
712	42.98	41.84	42.51	42.44	0.57
750	44.29	43.64	42.46	43.46	0.93
791	44.22	42.48	42.84	43.18	0.92

ANOVA

Source of variability	Sum of Squares (SS)	Degrees of freedom (df)	Mean sum of Squares (MS)	F-value	P-value	Critical F-value
between bottles	51.80749	19	2.726710	1.9958	0.032740	1.8529
within bottles	54.64876	40	1.366219			
total	106.45626	59				

The grand mean of the homogeneity study is 44.16 mg/kg. According to ISO Guide 35 the uncertainty between bottles $u_{bb} = S_{bb}$ is estimated as the greatest result of Eq. (1) and Eq. (2). Eq. (1) yields 0.6734 mg/kg and Eq. (2) yields 0.3191 mg/kg.

$$S_{bb} = \sqrt{\frac{(MS_{\text{among}} - MS_{\text{within}})}{n}} \quad (1)$$

$$S_{bb} = \sqrt{\frac{MS_{\text{within}}}{n}} \sqrt{\frac{2}{N(n-1)}} \quad (2)$$

where: n = Number of replicate determinations per sample
N = Number of bottles analysed

The relative value $u_{bb,r}$ is $0.6734/44.16 = 0.01523$.

Results of the homogeneity study on BAM-U025. SD – Standard deviation.

Bottle No.	Replicate			Mean (mg/kg)	SD (mg/kg)
	1 (mg/kg)	2 (mg/kg)	3 (mg/kg)		
13	249.84	248.40	261.95	253.39	7.44
49	260.00	243.98	240.58	248.19	10.37
80	246.47	243.34	244.48	244.76	1.58
115	240.83	238.15	255.56	244.85	9.37
148	238.20	254.88	247.59	246.89	8.36
182	235.14	238.97	260.67	244.92	13.77
217	229.12	244.44	253.41	242.32	12.28
253	246.74	263.72	251.39	253.95	8.77
278	243.15	240.44	241.48	241.69	1.37
306	247.84	245.99	266.33	253.39	11.24
344	260.44	256.45	247.84	254.91	6.44
369	256.75	237.29	249.71	247.92	9.85
403	220.37	251.52	253.06	241.65	18.44
446	228.62	226.10	254.01	236.24	15.44
478	226.01	222.76	258.06	235.61	19.51
526	221.91	238.99	281.71	247.54	30.81
568	222.45	258.02	235.10	238.52	18.03
597	278.82	268.09	251.82	266.24	13.59
621	249.68	257.99	256.67	254.78	4.47
655	266.56	268.64	255.12	263.44	7.28

ANOVA

Source of variability	Sum of Squares (SS)	Degrees of freedom (df)	Mean sum of Squares (MS)	F-value	P-value	Critical F-value
between bottles	3850.86263	19	202.67698	1.1586	0.3371078	1.8529
within bottles	6997.25402	40	174.93135			
total	10848.1166	59				

The grand mean of the homogeneity study is 248.061 mg/kg. According to ISO Guide 35 the uncertainty between bottles $u_{bb} = S_{bb}$ is estimated as the greatest result of Eq. (1) and Eq. (2). Eq. (1) yields 3.04 mg/kg and eq. (2) yields 3.61mg/kg.

$$S_{bb} = \sqrt{\frac{(MS_{\text{among}} - MS_{\text{within}})}{n}} \quad (1)$$

$$S_{bb} = \sqrt{\frac{MS_{\text{within}}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \quad (2)$$

where: n = Number of replicate determinations per sample
N = Number of bottles analysed

The relative value $u_{bb,r}$ is $3.611/248.061 = 0.0146$.

Results of the stability study

BAM-U024 (soil), AOX content in mg/kg

Bottle-Nr.	Treatment	Replicate	
		1	2
672	-80 °C	39	41
684	+ 4°C, 12 Months	41	38
694	+22 °C, 12 Months	40	39
700	+40 °C, 3 Months	40	39
702	+40 °C, 6 Months	42	39
704	+40 °C, 12 Months	39	41
708	+60 °C, 3 Months	39	38
710	+60 °C, 6 Months	37	36

BAM-U025 (sludge), AOX content in mg/kg

Bottle-Nr.	Treatment	Replicate	
		1	2
527	-80 °C	250	250
539	+ 4°C, 12 Months	250	230
549	+22 °C, 12 Months	260	260
555	+40 °C, 3 Months	260	250
557	+40 °C, 6 Months	280	240
559	+40 °C, 12 Months	270	270
563	+60 °C, 3 Months	260	250
565	+60 °C, 6 Months	280	280