

PRELIMINARY ANALYSIS OF A NEW IAEA LICHEN AQCS MATERIAL

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Abstract

Lichen with a higher content on interesting trace elements were analyzed by activation analysis and by X-RF measurements on pressed lichen samples. The activation analyses were performed in three different ways: Short-time AA in the Fast Irradiation & Measurement System. Up to 580mg of lichen were irradiated 5-300s in polyethylene containers. Single spectra and spectra of 6 samples were summed up and evaluated. Longer irradiation at the ASTRA-Reactor: 2h at $8E13/s\ cm^2$. 100-150mg of lichen were irradiated in quartz suprasil vials. Longer irradiation at the Institute's TRIGA-Reactor: 6-7h at $1.8E12/s\ cm^2$, sample size: 7-48g of lichen were irradiated in polyethylene containers and after irradiation transferred to new measurement containers and measured in a device constructed by Gwozdz. The X-RF analysis was performed with a Spectrace 5000 energy dispersive X-ray fluorescence analyzer with a rhodium anode tube for excitation. From the activation analyses, the following elements were determined: Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Hf, Hg, I, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Rb, Sb, Sc, Se, Sr, Ta, Tb, Th, Ti, U, V, Yb, Zn. From the X-RF measurements, the elements Ag, Al, Ba, Br, Ca, Cd, Cu, Fe, I, K, Mg, Mn, P, Pb, Rb, S, Sb, Si, Sn, Sr, Ti, Y, Zn, and Zr were evaluated. From the X-RF data as well as from the AA-data of samples of different weight it is apparent that milling to a particle size of 200m is not sufficient for all elements, especially not for gold, cadmium, and cobalt which may be present as nuggets or accessory heavy minerals. It is therefore advisable to mill the sample to a particle size which is an order of magnitude smaller and remove the not adhering dust, even if this lowers the content of these elements.

1. INTRODUCTION

Lichen can be used as a monitor for aerosols, as it integrates dust over a longer period of time. Therefore, the IAEA has introduced a standard reference material IAEA 336. For the preparation of a more contaminated lichen standard material, the region near Bleiberg/Carinthia seemed a suitable lichen source, as lead was mined and smeltered there for a long time. In autumn 1995 a preliminary search showed that lichen (mainly *pseudevernia furfuracea*) is available in sufficient quantity in this region. Analyses of several samples by short-time activation analysis indeed showed higher contents of interesting elements. So 24 kg of lichen were collected there in September 1996. A representative sample of lichen and its dust was crushed after drying in an agate mill to a particle size of about 200 m. At least parts of the lichen sample must have had a residence time of more than 10 years, as measured by the $^{137}Cs/^{134}Cs$ ratio, which showed a surplus of ^{137}Cs .

2. SAMPLE

2.1 Collection of lichen

About 24kg lichen (mainly *pseudevernia furfuracea*) were collected at different places around Bleiberg: 1) On Dobratsch in a height of 1400-1600m in the main wind direction of the lead mining tower. 2) On Dobratsch near the lower cable car station at about 1000m, in the main wind direction. 3) Facing Dobratsch, at a distance of 2km from the mining tower at about 1400m. 4) South of Kreuth, on the western part of Dobratsch exposed to the south at 1300m. 5) Southeast of Arnoldstein near the Austrian/Slovenian border in the main wind direction from the lead processing plant at a height of about 1000 m.

2.2 Preparation

The lichen was manually sorted by the IAEA crew in Seibersdorf and the lichen containing adhering bark particles were separated. This procedure was performed on all the collected lichen. The lichen with adhering bark particles was selected for a preliminary analysis. The lichen was manually selected from bark particles, needles, and dust. **Lichen and dust** were combined and milled in an agate mill until it passed a 200mm sieve, and mixed by shaking 6h in a plastic container for analysis. Bark particles and needles were separated for an activation analysis.

2.3 Residence time evaluation

A rough residence time determination of materials exposed to aerosols is possible by measurement of the activity of the Cs-radionuclides which were emitted from the Chernobyl accident: The Cs-137 activity (half life of 30y) is compared with Cs-134 activity (half life 2.07y). If Cs-134 is found in the sample it must stem partly from the Chernobyl accident on 1-May-86. If a surplus of Cs-137 appears, a remaining activity from the bomb-test series must be present, so the mean age of the measured sample must date back to at least 1986. Milkpowder is a suitable reference material to obtain a good approximation for the Cs-isotope ratio at the time of the Chernobyl accident as milk is produced by cows fed with grass of the same year, in which a memory effect of Cs-137 is very unlikely. 500g corresponding to 800ml of the milk powder was measured in a Marinelli beaker on a 30% Ge(Li)-detector. The calculated Cs-137/134 ratio at the Chernobyl accident time 1-MAY-86 was **1.702 +/- 0.018**.

To verify that the mean age of the lichen sample is older than 1986 its activity was measured: 500g corresponding to 800ml were measured in the Marinelli beaker. The Cs-137 / Cs-134 ratio calculated for 1-MAY-86 was found to be **1.808 +/- 0.058**. The small surplus of Cs-137 showed that some amount of Cs-137 was left from the atomic bomb test series, so that some of the measured lichen must be more than 10 years old. This is important as the lead mine was closed down around this date.

3. LICHEN ANALYSIS

The samples were analyzed by activation analyses and XRF-measurements on pressed lichen samples. Bark and needle samples were only measured by activation analysis.

3.1 Activation analysis

These analyses were performed in three different ways:

- 1) Short-time AA in the **Fast Irradiation & Measurement System FIMS**. Up to 580mg of sample were irradiated 5-300s in polyethylene containers. Single spectra and spectra of 6 samples were summed up and evaluated.
- 2) Longer irradiation at the ASTRA-Reactor: 2h at $8E13/s\ cm^2$. 100-150mg of the sample were irradiated in quartz suprasil vials (lichen, bark and needles).
- 3) Longer irradiation at the Institute's TRIGA Reactor: 6-7h at $1.8E12/s\ cm^2$ sample size: 7-48g of lichen samples were irradiated in polyethylene containers and transferred to new measurement containers. Five 10g-samples were measured to test the homogeneity. The measurements were performed on different HP-Ge detectors: in FIMS, a 15% detector with resetting preamplifier was used, which feeds the signal into a newly constructed digital preloaded filter amplifier [1]. The signals pass a dual LFC system for deadtime and pile up correction, and are then stored by an ACCUSPEC B chart on the hard disk of a 386PC. Three spectra with successively increasing measurement time were registered.

TABLE Ia. ANALYSIS OF LICHEN COLLECTED AT BLEIBERG, CARINTHIA, AUSTRIA

ELEMENT/UNIT	Short time AA	ASTRA	TRIGA	TRIGA	Comparator	Comparator
					Orchard/Citrus I. XRF	Pine Needles XRF
SAMPLE SIZE	0.3-0.5g	0.10-0.14 g	5.5-8.8g	47.9g	2.2-5.5g pellets	2.2-5.5g pellets
P mg/kg					865+/-18	
Pb mg/kg					107.7+/-15.2	
Rb mg/kg		17.9+/-1.9	22.2+/-1.0	24.2+/-0.2	25.0+/-2.0	18.2+/-1.4
S mg/kg					2213+/-26	
Sb mg/kg		0.685+/-0.011	1.97+/-0.021	1.73+/-0.02	1.52+/-0.34	
Sc mg/kg		0.436+/-0.010	0.398+/-0.002	0.415+/-0.001		
Se mg/kg			1.60+/-0.36	1.55+/-0.06	4974+/-122	
Si mg/kg					3.19+/-0.58	
Sn mg/kg					10.5+/-0.65	7.56+/-0.47
Sr mg/kg		11.9+/-0.67				
Ta mg/kg		0.048+/-0.05				
Tb ng/kg		33+/-8				
Th mg/kg		0.36+/-0.07			161+/-20	111+/-14
Ti mg/kg	193+/-12					
Tm mg/kg						
U mg/kg			(0.122)Np239			
V mg/kg	7.80+/-0.02				2.45+/-0.58	1.69+/-0.40
Y mg/kg						
Yb ng/kg			105+/-10	97.7+/-2.1	176.2+/-4.6	120.4+/-3.1
Zn mg/kg		121+/-2	112+/-2	118+/-1	8.96+/-2.3	5.91+/-1.52
Zr mg/kg						
Ag mg/kg		0.11+/-0.03	0.17+/-0.02	0.13+/-0.01	0.57+/-0.14	
Al mg/kg	2024+/-10				1360+/-85	
As mg/kg			1.44+/-0.10	1.24+/-0.03		
Au ng/kg		18+/-2	118+/-5	12.0+/-0.1		
Ba mg/kg	72+/-13	65.3+/-7.1	77.1+/-0.9	75.8+/-0.6	40.4+/-6.2	
Br mg/kg	29.4+/-2.1	24.3+/-1.1	29.2+/-0.1	27.3+/-1.1	32.5+/-1.9	24.0+/-1.4
Ca mg/kg	6250+/-150	6480+/-100	5000+/-300	6500+/-300	8750+/-78	5651+/-51
Cd mg/kg			1.3+/-0.4	0.72+/-0.09	0.62+/-0.19	
Ce mg/kg		2.00+/-0.06	2.20+/-0.30	2.22+/-0.01		
Cl mg/kg	2940+/-30					
Co mg/kg		0.485+/-0.11	1.07+/-0.04	1.18+/-0.03		
Cr mg/kg		9.80+/-0.12	11.9+/-0.65	11.7+/-0.01		
Cs mg/kg		0.55+/-0.05	0.62+/-0.05	0.72+/-0.02		
Cu mg/kg	26.3+/-3.8				33.5+/-19.2	22.4+/-12.8
Dy mg/kg	0.135+/-0.014					
Eu ng/kg		46+/-4	43+/-3	46.1+/-0.8		
Fe mg/kg		1846+/-40	1888+/-55	1912+/-39	1957+/-20	1267+/-13
Hf mg/kg	0.242+/-0.002	0.214+/-0.020	0.240+/-0.006	0.236+/-0.002		
Hg mg/kg		0.82+/-0.02	0.70+/-0.05	0.936+/-0.009		
I mg/kg	6.49+/-0.49				4.97+/-0.85	
K mg/kg			3650+/-300	3110+/-200	3447+/-29	2842+/-24
La mg/kg		2.10+/-0.42	2.13+/-0.01	2.10+/-0.01		
Lu ng/kg			8.62+/-0.26	8.66+/-0.08		
Mg mg/kg	1335+/-152				540+/-51	
Mn mg/kg	69.3+/-7.7				106.8+/-7.9	69.2+/-5.2
Mo mg/kg			16.2+/-1.0	12.0+/-3.0		
Na mg/kg	225+/-10		262+/-10	232.4+/-5.0		
Nd mg/kg		1.43+/-0.08				
Ni mg/kg		11.7+/-2.7	15.8+/-1.2	11.9+/-1.0		

The measurements of the samples irradiated at the ASTRA-reactor were measured at least twice after appropriate decay time, by an electronic equipment corresponding to that described above, but stored on 486 PC. Some measurements were performed on a well-type detector [2].

The large samples irradiated at the Institute's TRIGA-reactor were measured with the same system. The peak areas of all spectra were evaluated by a modified PEAK program, developed for the dual LFC- systems [3].

3.2 XRF-analysis

The measurements were performed with a Spectrace 5000 energy dispersive X-ray fluorescence analyzer with a rhodium anode tube for excitation. 10 samples, dried at 60°C for 24h, were pressed at about 10 t to pellets having an area density between 0.316 and 0.769 g/cm². Assuming similar properties of the matrices, NBS SRM 1572 (Citrus Leaves) and NBS SRM 1571 (Orchard Leaves) were used for one set of calibration data. Another set was based on NBS SRM 1575 (Pine Needles). The elements Ti, Mn, Fe, Cu, Zn, Br, Rb, Sr, Y, Zr and Pb were measured at 40 kV, 0.06mA, with a thick Pd-filter in the primary beam, for 1000 s life time, the elements Mg, Al, Si, P, S, K, and Ca at 7kV and 0.35mA under vacuum conditions, for 1000 s life time, the elements Ag, Cd, Sn, Sb, I, and Ba at 50kV, 0.35mA, and a Cu-filter in the primary beam, for 2000 s life time. The net peak area of the fluorescence lines was extracted from the measured spectra by the AXIL-peak fitting routine. For the conversion to concentrations the program "Direct comparison of count rates " was used (software package QXAS, Version 3.5.).

4. RESULTS

The data of the lichen analyses are summarized in Table Ia and Ib. The results of the analysis of small lichen-, bark-, and needle- samples are given in Table II.

TABLE II. LICHEN, BARK, NEEDLES COLLECTED AT BLEIBERG, KÄRNTEN, AUSTRIA

ELEMENT/UNIT	LICHEN	BARK	NEEDLES	COMPARATOR	DATA USED
SAMPLE SIZE	0.136	0.101	0.113	[g]	
Au ng/kg	18+/-2	0.26	7.3	IAEA 336	3.31+/-0.03
Ba mg/kg	65.3+/-7.1	28.6	11.8	NBS 1632a	130.
Br mg/kg	24,3+/-1.1	15.4	6.1	IAEA 336	13.04+/-0.52
Ca mg/kg	6686+/-285	9558.	13330.	- "- -	2870+/-124
Ce mg/kg	2.00+/-0.06	2.17	0.33	- "- -	1.28+/-29.4
Co mg/kg	0.48+/-11	0.33	1.09.	- "- -	0.295+/-0.014
Cr mg/kg	9.80+/-0.12	6.25	1.97	BCR 176	863 +/-30
Cs mg/kg	0.55+/-0.05	0.22	0.11	IAEA 336	109.7+/-2.2
Eu ng/kg	46+/-4	24.9	<6	- "- -	22.5+/-1.2
Fe mg/kg	1846+/-40	878.	1607.5	- "- -	430.4+/-10.1
Hf mg/kg	0.214+/-0.020	0.107	0.026	- "- -	57.6+/-1.8
Hg mg/kg	0.82+/-0.02	0.46	0.20	Hg-Std	50.
La mg/kg	2.10+/-0.42	1.2	0.29	IAEA 336	0.671+/-0.034
Lu ng/kg	19.7+/-0.99	13.8	1.8	- "- -	6.71 +/- 1.01
Nd mg/kg	1.43+/-0.08	3.14	1.04	- "- -	524.5+/-0.50
Rb mg/kg	17.9+/-1.9	11.4	17.5	BCR 1	133+/-23
Sb mg/kg	0.69+/-0.01	0.87+/-0.04	<0.05	IAEA 336	0.0736+/-0.003
Sc mg/kg	0.436+/-0.009	0.223+/-0.029	0.029	- "- -	0.172+/-0.005
Sr mg/kg	11.9+/-0.67	27.9	20.6	- "- -	9.59+/-0.33
Th mg/kg	0.36+/-0.07	0.193	0.024	- "- -	0.142+/-0.005
Zn mg/kg	121+/-2	134.	61.9	- "- -	30.25+/-0.75

5. DISCUSSION OF RESULTS

The values +/- correspond to the error of the mean values of at least two measurements of the same or of different samples. Some of the results by short-time AA were obtained by evaluation of six summed spectra. The comparators for the data evaluation were synthetic multi-element standards as

well as NBS- and IAEA- standards: NBS1632a (Bituminous Coal), NBS1575 (Pine Needles), NBS1570 (Spinach), IAEA336 (Lichen), Animal Bone, and BCR176 (City Waste Incineration Ash). Most data correspond to GLADNEY's compilation listed in [4]. However, the value of chromium in IAEA336 is about a factor 3 too low compared with single element standards, BCR176, NBS 1632a, NBS 1575, and NBS 1575.

The homogeneity of the sample for some elements is not sufficient as seen from the results of gold, cadmium, and cobalt with samples of different size. These elements may be present as nuggets or accessory heavy minerals. The 47.9g sample, however, can be used as a good approximation for the total content of these elements.

Some major divergent data of Mg and Al between activation analysis and XRF-fluorescence measurements may be due to the fact that these lines are just on the lower Z-limit of the method. The differences between the data obtained with different comparators show that even NBS SRM would require harmonizing.

6. CONCLUSIONS

With few exceptions (Na, Mn, Sr) the content of elements in the lichen collected at Bleiberg is a factor of about 2-10 higher than in the lichen standard IAEA 336. Provided the Bleiberg-lichen is milled to a smaller particle size, it will supplement the IAEA 336 lichen standard for higher element content, so that a lichen standard for strongly contaminated areas is available.

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