Altitude influence of elemental distribution in grass from Rila mountain

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- **I. Introduction**
- The application of modern instrumental methods to the determination of trace elements in environmental samples has promoted the better understanding of the role of this elements. The acquainting with the concentrations of heavy metals and toxic elements gives us the opportunity for investigation of the distribution and dynamics of chemical elements accumulation in flora and fauna and their passing over the trophic chains and also for evaluation of antropogenic influence of toxic elements and technogenic transportation on the ecosystems.
- The energy dispersive X-ray fluorescence analysis is one of the well known analytical methods as a powerful analytical tool for the qualitative and quantitative determination of almost all chemical elements in a sample, first of all as a rapid and reliable method.

- **II. Principles and instrumentation**
- In the EDXRF method, the sample, to be analysed is excited with electromagnetic radiation of sufficient energy. This leads to the ejection of electrons from the inner shells of the atoms present. Each vacancy is immediately filled up by an electron from an outer shell while the difference in energy between the two levels is generally released in the form of an X-ray. The energy of the emitted X-ray is characteristic for the ionised element, and from the intensities of the different characteristic X-rays in the spectrum, the concentration of the elements in the sample can be deduced. X- ray fluorescence requires the source of radiation, the sample, which is irradiated and the detection system. With these the spectrometer is complete and through computer support all necessary calculations to transfer the intensities into concentrations and to identify the elements can be carried out from the measured spectrum.
- The power of this analytical instrument is due to the energy dispersive detector, the simultaneous determination of all elements. Information is obtained rapidly and no element, which is present can be overlooked. For standard excitation the lower detection limits are in the range µg/g (ppm). This is sufficient for many applications, but for some environmental problems these detection levels are too high. Recent developments for solving this problems are the application of total reflection and the introduction of synchrotron radiation sources for excitation

- **III. Sample and sample preparation**
- The best procedure for sample preparation is to leave the sample as it is, but in many cases this is unrealistic. Any process to transfer the sample on a substrate or preparation needs safe treatment so as to guarantee that the processed sample is representative of the original. Homogeneity of the sample and contamination free sample preparation are the basic requirements in each technique. In particular, environmental samples, which we investigate in our lab are soils, sediments, leaves, needles, grass, moss, lichen, fishes, small mammals. In order to minimize the error from sample preparation we use only a drying and grinding procedure. An amount of about 300g from the sample is dried in microwave oven for 10 minutes. Then this sample is ground to a mesh side about 0.1mm and homogenised. An amount of 30g from the plants and biological samples and 50g from soils and sediments are pressed in a specialised sample carrier. Particular difficulties occurs, when very small amount from the sample are available, as in the case of internal tissue of fishes and small mammals. In this case an approximation curve intensity versus sample mass is established for normalisation of obtained characteristic X-ray intensities

- **IV. Instrumentation**
- Two spectrometric systems are available in our lab for X-ray analyses. The first one is equipped with Si(Li) detector with 12.5 μm Be window and 180 eV energy resolution at 5.9 keV Mn-K_α line. The data are acquired with a multi-channel analyzer, interfaced to a personal computer, that applies specialized software for spectra processing. This system is combined with an exciting head, based on an annular source Am^{241} with activity 3.7 GBq and three types of secondary targets in two excitation mode - transition and reflection in order to select the desired exciting energy - namely the characteristic line of Mo (17.44 keV), Sn (25.19 keV) and Dy (45.98 keV). For determination of heavy elements, which are essential for biology the system use the Dy secondary target, that allows detection of elements down to the Z=56. This construction permits the measurement of great number of elements with a high sensitivity by achieving the desirable experimental conditions of low background level and at a high count rate.
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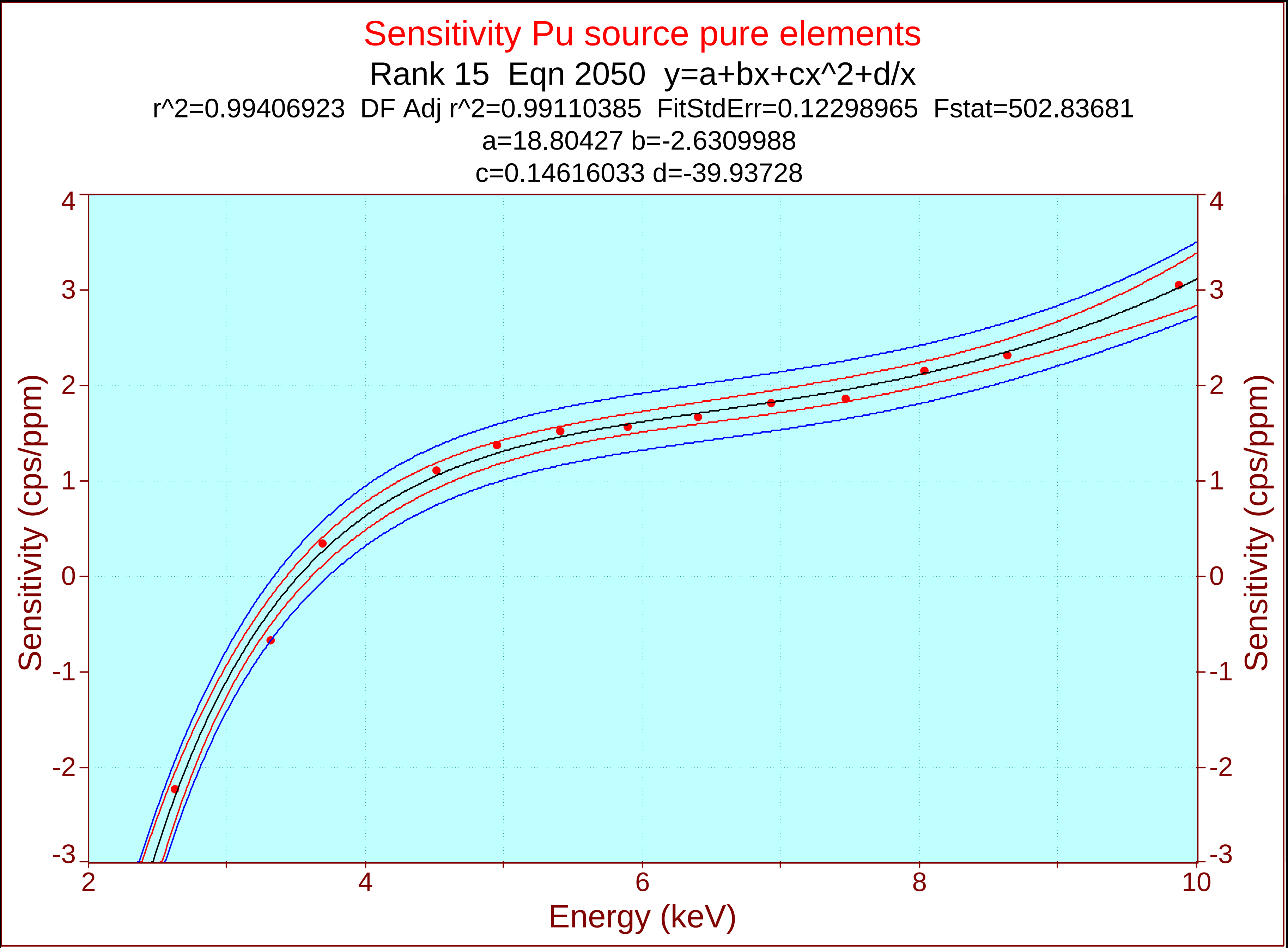
- The second system is equipped specially for light element analysis with Si(Li) detector with 12.5 μm Be window and 160 eV energy resolution for 5.9 keV Mn-K_{α} line. An exciting head, especially designed for low Z elements determination is equipped with three radionuclide sources Fe^{55} . In the case of this construction, the distances source-sample and sample-detector are greatly reduced and optimized, which allows elements with atomic number Z=13 to 25 to be analyzed.
- During the measurements of zoological samples, traces from very essential for biology elements like Cu, Zn, Mn, Pb were occurred. To become higher sensitivity and lower detection limit for these elements another exciting source Pu^{238} is built in the same head (fig. 3). It's energy of 13.613 keV is very suitable for exciting of elements with Z=22 to 35. In this way the all range of Z from 13 to 82 is covered and each sample can be measured with this three kind of excitation.

- **V. Spectrum processing**
- To obtain results the measured spectra must be evaluated as to line energies and line intensities, with only the net intensity used for quantification. The correctness with which the peak areas for the analyzed elements are determined is of crucial importance in order to obtain accurate and reliable results for their amounts. Different methods for energy-dispersive X-ray spectra processing have been investigated and now in software package three different methods for peak area determination are included - namely total peak area, linear and non-linear least square algorithms, resolution enhancement procedures.

- **VI . Calibration**
- A set of international standards, such as lake sediment IAEA SL-1, soil IAEA Soil-7, air born dust BCR-128. These standards are applied for soil calibration curve. A Belgian standard FCG-15 is applied for verification of these curves. The obtained results are in good agreement with the reference concentrations for the standard.
- For the exciting head with Fe^{55} sources a set from different plant standards - Bowen's kale, IAEA V10-Hay, orchard leaves were used for matrix correction, because of higher amounts of the light element concentration - K, Ca, Cl etc. For the estimation of the sensitivity curves for animal spacies three other IAEA's standards (horse kidney, coppepod and fish flash) were applied.
- Once the correlation between intensity and concentrations is found, comparable sample types, measured under same conditions can be quantified. At trace levels the XRF techniques provides a direct proportionality between analyte line net intensity and its concentration. This holds for homogenous sample of a given matrix and either of constant or infinite thickness, i.e. of constant mass. In this way, when the net intensities of the analytical elements are found the unknown elemental concentrations can be calculated.



Sensitivity Pu source pure elements

Rank 15 Eqn 2050 y=a+bx+cx^2+d/x

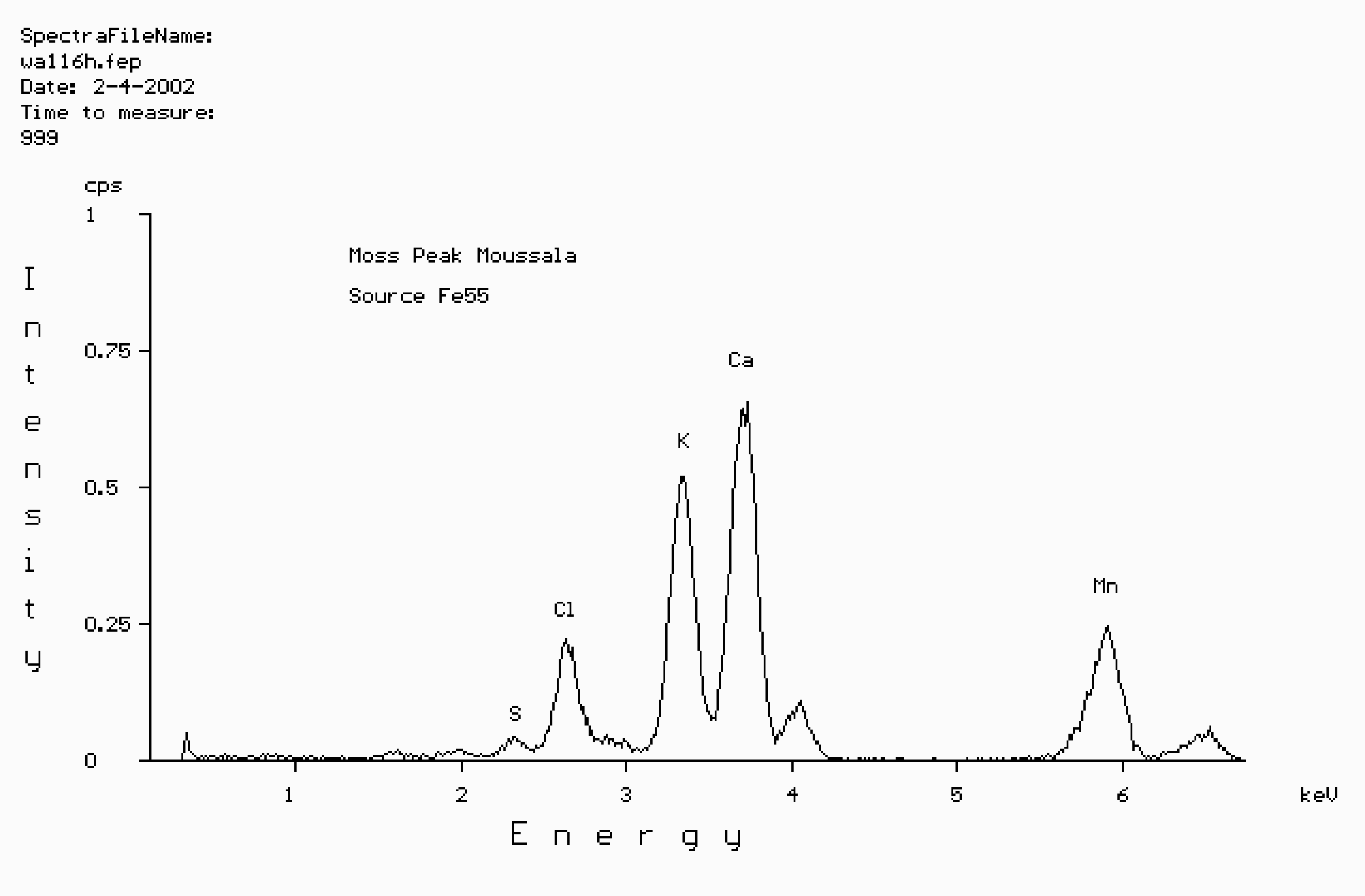
r^2=0.99406923 DF Adj r^2=0.99110385 FitStdErr=0.12298965 Fstat=502.83681

a=18.80427 b=-2.6309988

c=0.14616033 d=-39.93728

- **VII. Accuracy, errors and detection limits**
- The total error of the analysis consists of many errors, which can be provocate by: measurement of the intensity, reproducibility of the sample preparation and conversion of intensity into concentration. The total relative error of a 7 - 10% is estimated during the calibration procedure as a standard deviation error of a previously prepared and analyzed standards with known element concentrations.
- The detection limits (DL) (the minimum amount, that can be analyzed) are determined by the sensitivity and by the background in the X-ray spectrum. The use of three kinds of excitation give us the opportunity to reach detection limit levels, which are enough for environmental control and monitoring purposes. With a new technique of total reflection XRF a drastically decrease of this values is possible.


GT
GT



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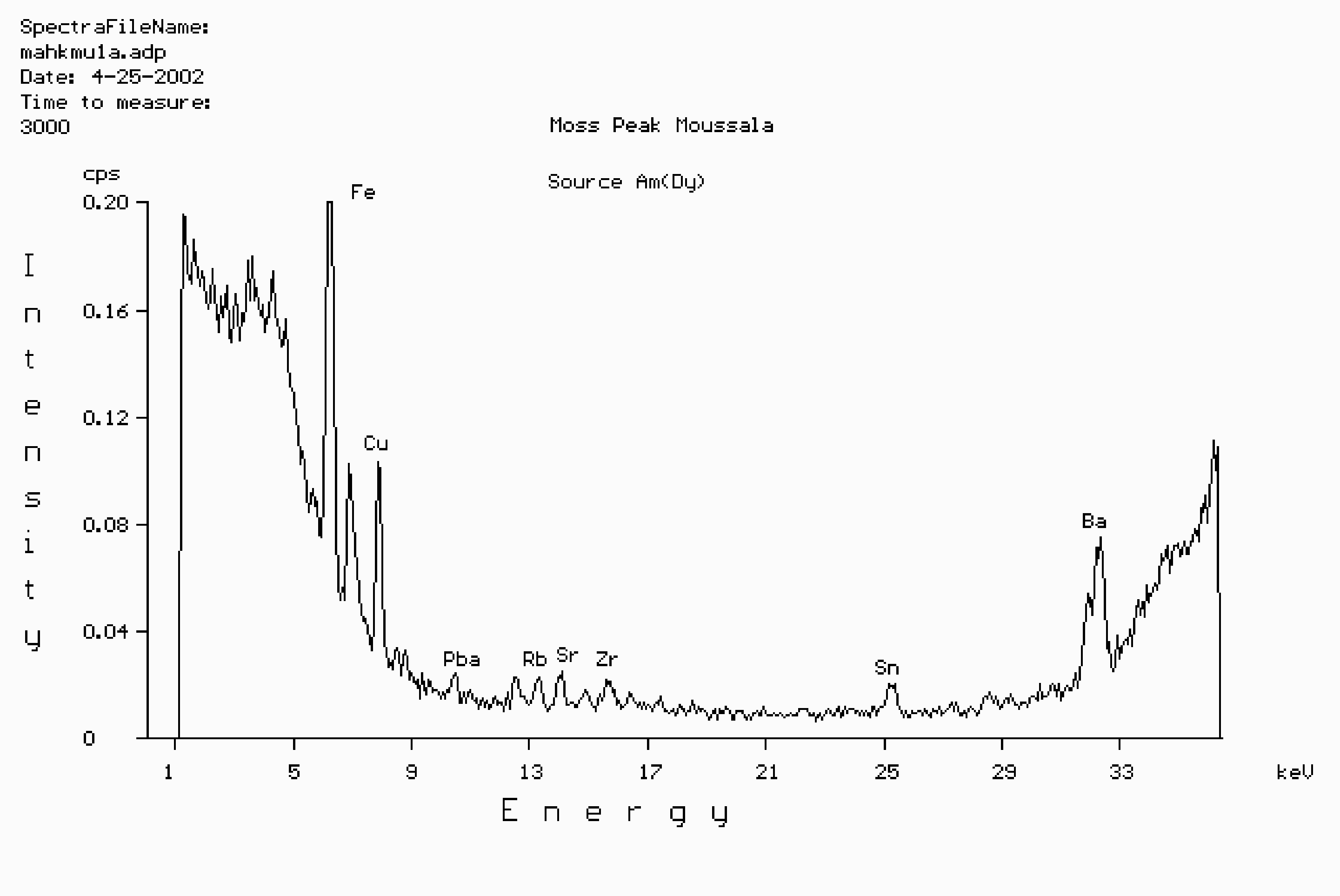
Moss Peak Moussala

Source Fe55


ORTEC
EG&G ORTEC



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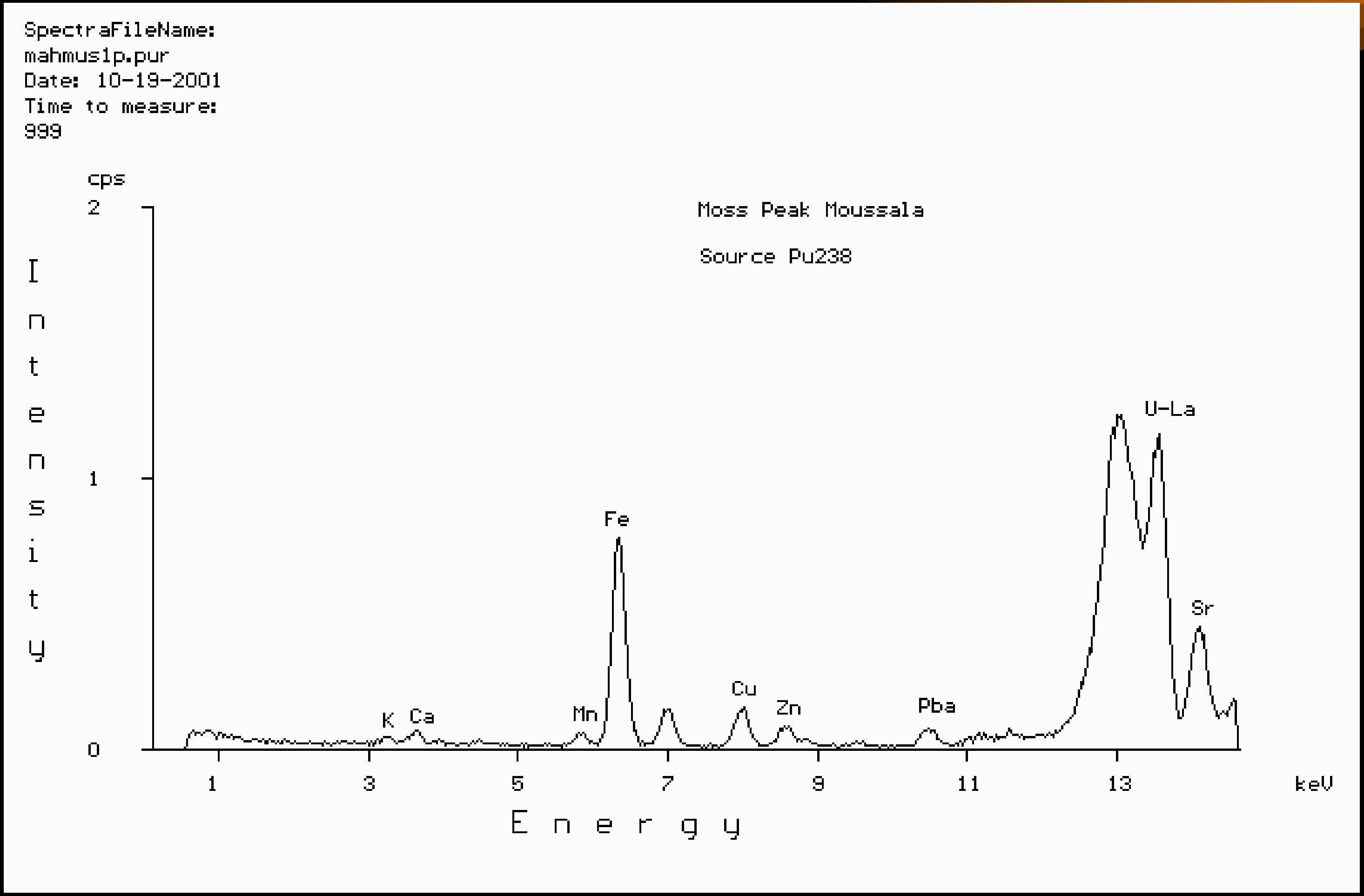
Moss Peak Moussala

Source Am(Dy)



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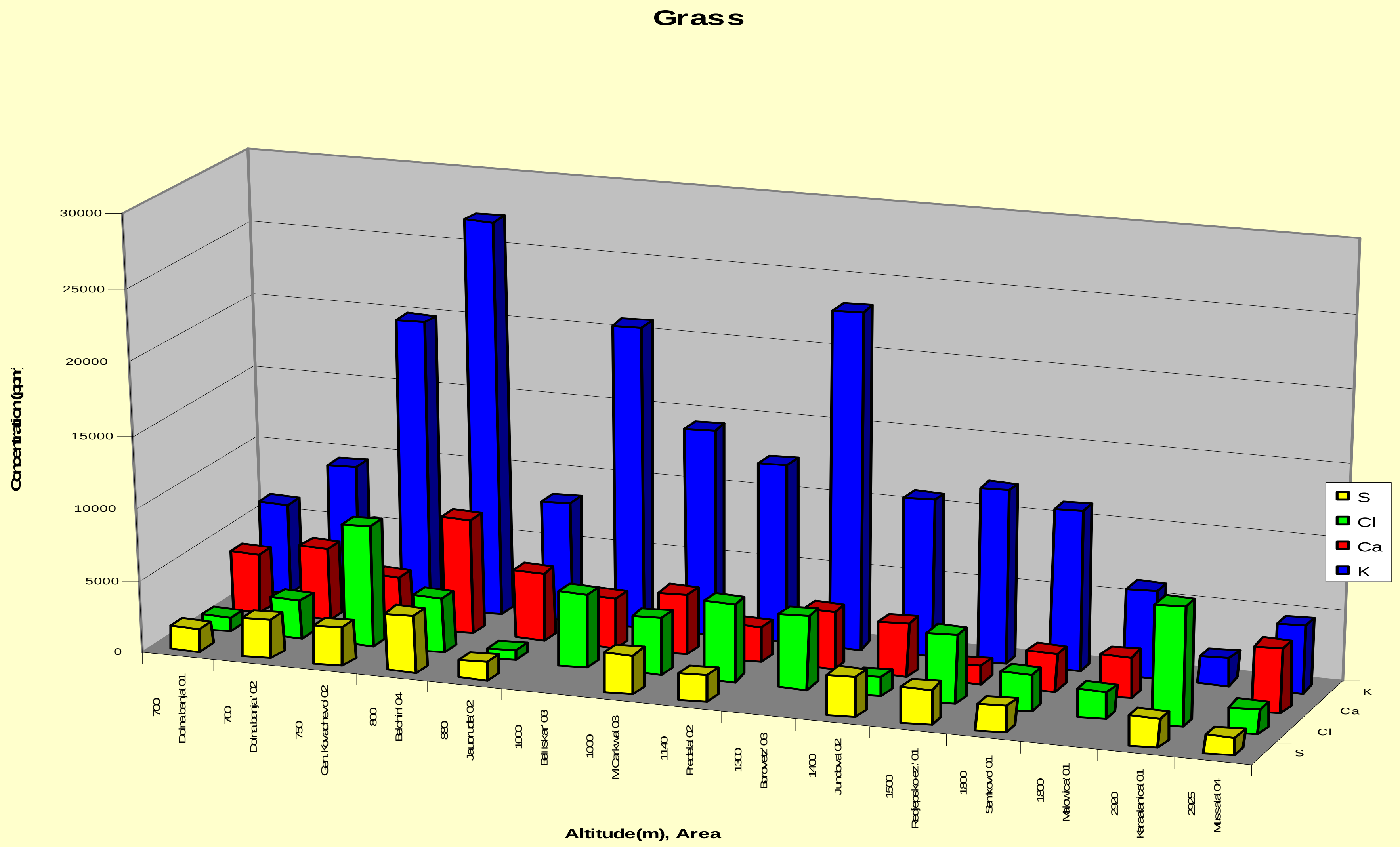
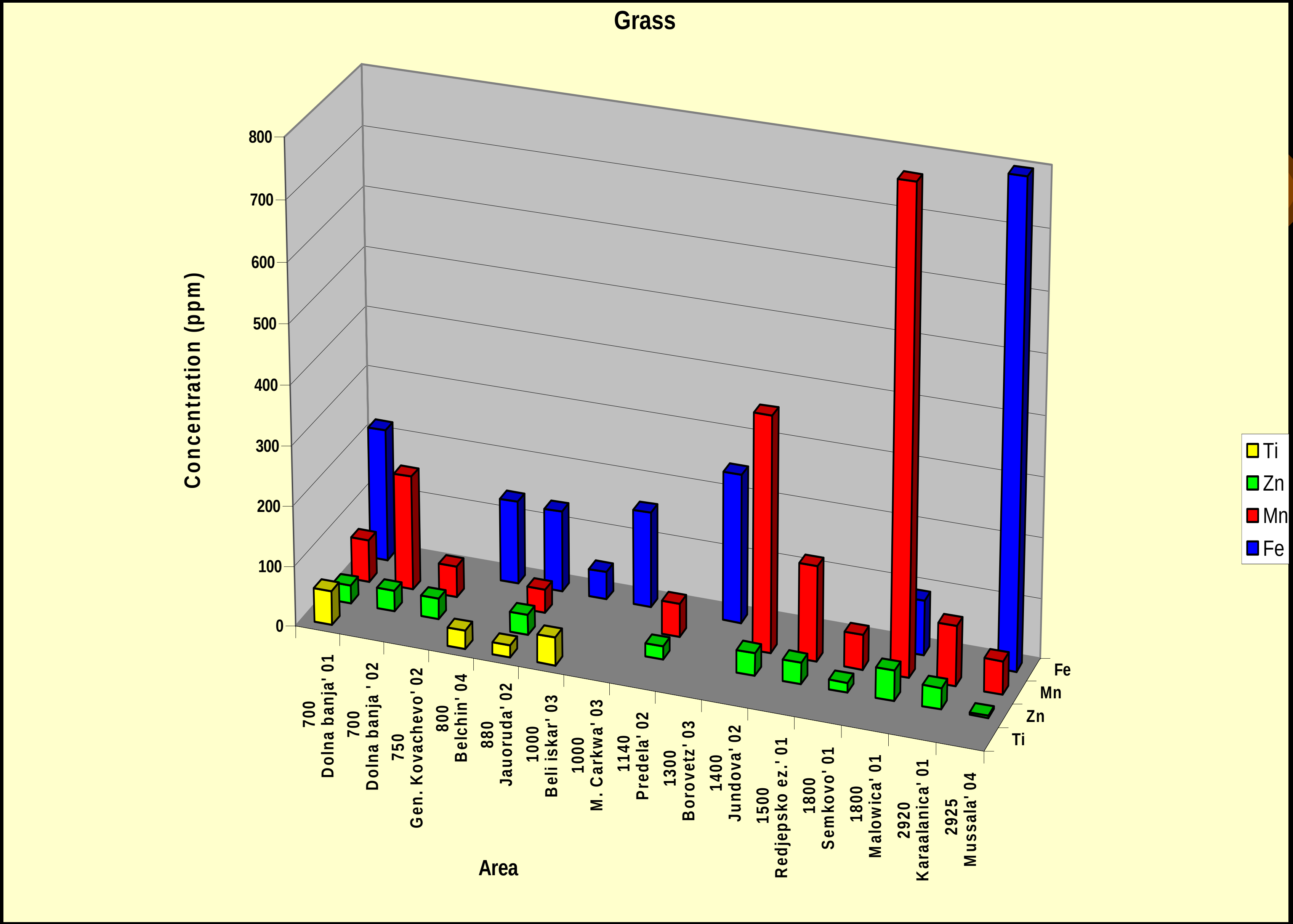
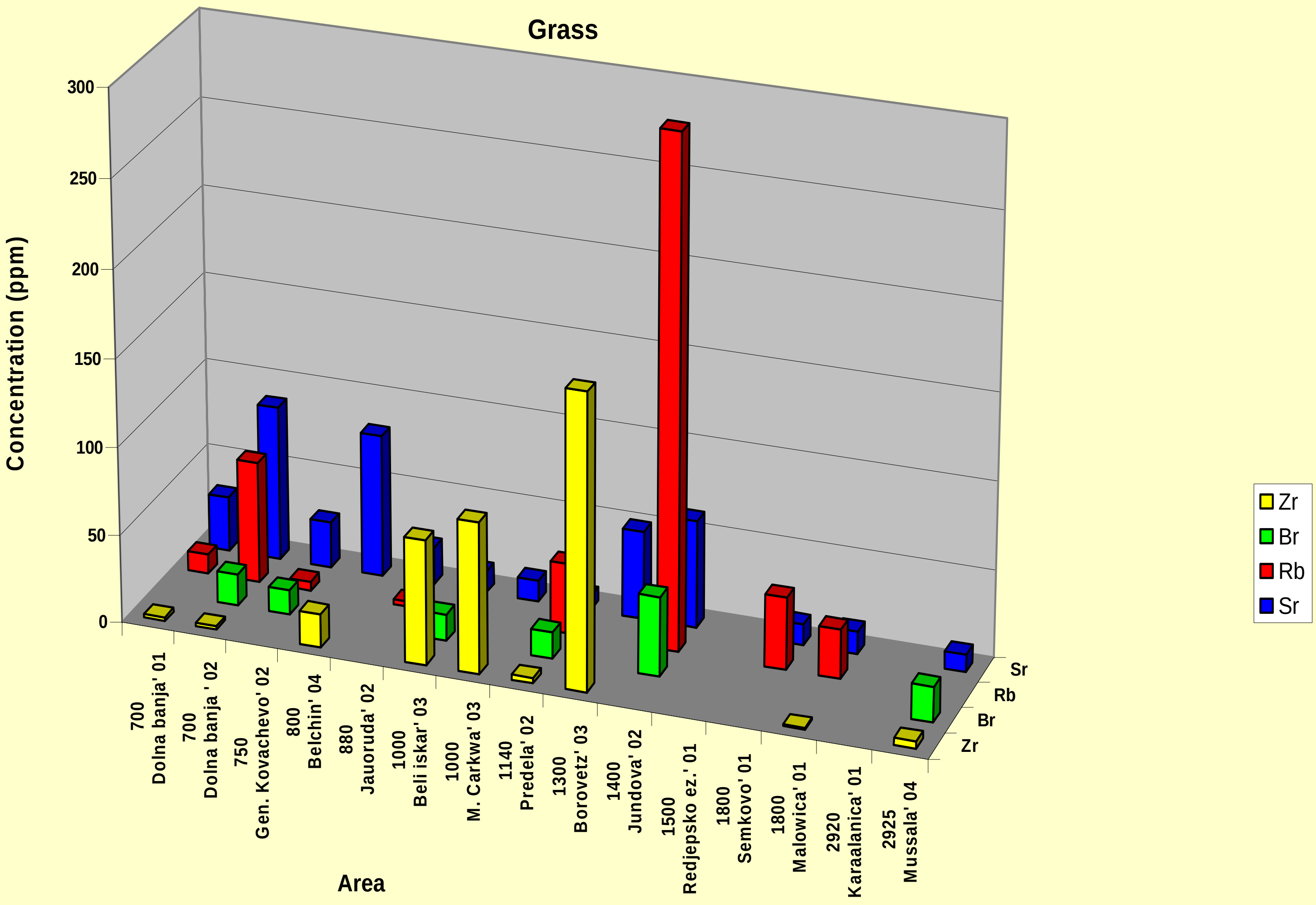
Moss Peak Moussala

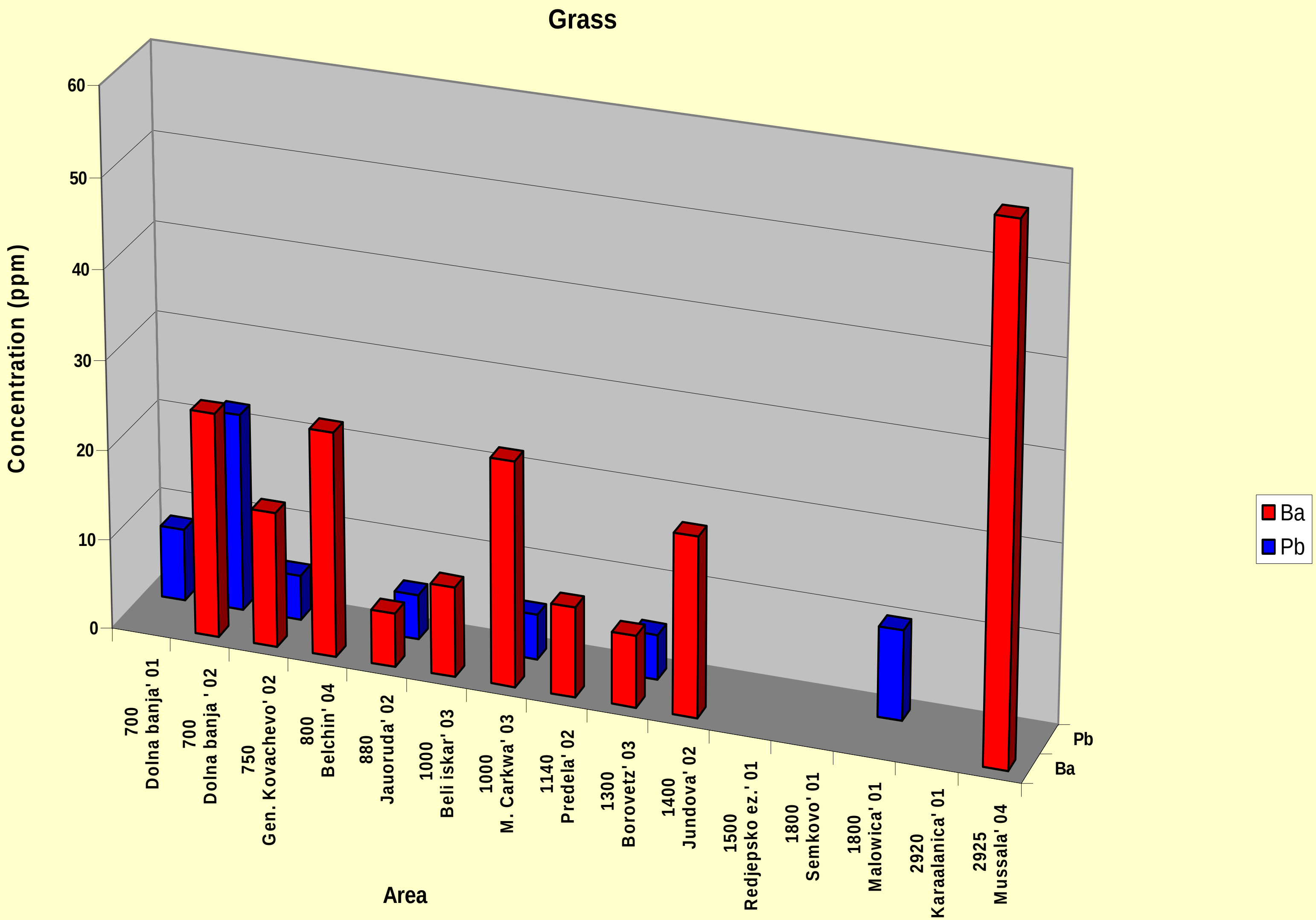
Source Pu238

Element		**SAMPLE CODE**									
Z		**trvbli3**		**trvbor3**		**trvmcr3**		**trvbel4**		**trvmus4**	
		Value	+/-	**Value**	+/-	**Value**	+/-	**Value**	+/-	**Value**	+/-
Al	%										
Si	%							17760	300	15330	350
P	(ppm)	3250	300	3190	300	3080	300	5330	600	1700	150
S	(ppm)					2760	250	3980	500	1260	100
Cl	(ppm)	5110	250	5050	100	3950	100	3860	100	1700	100
K	(ppm)	20950	480	23270	550	14270	350	27270	600	4640	150
Ca	(ppm)	3475	30	4010	40	4210	40	8020	350	4500	40
Ti	(ppm)	47	2					31	2		
V	(ppm)										
Cr	(ppm)										
Mn	(ppm)	46	4	248	8	159	7	139	7	55	5
Fe	(ppm)	104	2	108	4	104	5	221	10	1167	58
Ni	(ppm)	9	1	4	1	3	1				
Cu	(ppm)									4	1
Zn	(ppm)	19	1	27	1	34	3	24	2	31	3
Ga	(ppm)										
As	(ppm)	15	2							20	3
Se	(ppm)										
Br	(ppm)	12	2	50	5	12	2	81	7	10	2
Rb	(ppm)	71	2	168	8	86	4	19	2	4	1
Sr	(ppm)			42	6	29	2	40	3	20	2
Y	(ppm)										
Zr	(ppm)	2	1					3	1	7	1
Nb	(ppm)										
Mo	(ppm)										
Ag	(ppm)					1	1				
Cd	(ppm)					1	1				
Cs	(ppm)							3	1		
Ba	(ppm)	10	2	8	2	25	2	25	3	59	6
Hg	(ppm)										
Pb	(ppm)			5	2	5	2				
Weight,g		7,69		15,26		16		15,2		17	
Sample		grass		grass		grass		grass		grass	


Grass
Concentration (ppm)
30000
25000
20000
15000
10000
5000
0
700 Dolna banja' 01
700 Dolna banja' 02
750 Gen.Kovachevo' 02
800 Belchin' 04
880 Jauoruda' 02
1000 Beli iskar' 03
1000 M.Carkva' 03
1140 Predela' 02
1300 Borovetz' 03
1400 Jundova' 02
1500 Redjepsko ez.' 01
1800 Semkovo' 01
1800 Malovica' 01
2920 Karaalanica' 01
2925 Mussala' 04
Altitude(m), Area
K
Ca
Cl
S
🟨 S
🟩 Cl
🟥 Ca
🟦 K


Grass
Concentration (ppm)
800
700
600
500
400
300
200
100
0
700 Dolna banja' 01
700 Dolna banja ' 02
750 Gen. Kovachevo' 02
800 Belchin' 04
880 Jauoruda' 02
1000 Beli iskar' 03
1000 M. Carkwa' 03
1140 Predela' 02
1300 Borovetz' 03
1400 Jundova' 02
1500 Redjepsko ez.' 01
1800 Semkovo' 01
1800 Malowica' 01
2920 Karaalanica' 01
2925 Mussala' 04
Area
Fe
Mn
Zn
Ti
Ti
Zn
Mn
Fe


Grass
Concentration (ppm)
300
250
200
150
100
50
0
700 Dolna banja' 01
700 Dolna banja ' 02
750 Gen. Kovachevo' 02
800 Belchin' 04
880 Jauoruda' 02
1000 Beli iskar' 03
1000 M. Carkwa' 03
1140 Predela' 02
1300 Borovetz' 03
1400 Jundova' 02
1500 Redjepsko ez.' 01
1800 Semkovo' 01
1800 Malowica' 01
2920 Karaalanica' 01
2925 Mussala' 04
Area
Sr
Rb
Br
Zr
Zr
Br
Rb
Sr


Grass
Concentration (ppm)
60
50
40
30
20
10
0
700 Dolna banja' 01
700 Dolna banja ' 02
750 Gen. Kovachevo' 02
800 Belchin' 04
880 Jauoruda' 02
1000 Beli iskar' 03
1000 M. Carkwa' 03
1140 Predela' 02
1300 Borovetz' 03
1400 Jundova' 02
1500 Redjepsko ez.' 01
1800 Semkovo' 01
1800 Malowica' 01
2920 Karaalanica' 01
2925 Mussala' 04
Area
Pb
Ba
🟥 Ba
🟦 Pb

- **VIII. Conclusions**
- EDXRF is capable of detecting traces of almost all elements of the periodic system. The method enables fast, non-destructive direct analyses without lengthy sample pre-treatment and is well suited for environmental investigations because of its sensitivity and lower detection limits achieved and also because of the rapid and simultaneous acquisition of information on the elements present. The software available permits quantitative determination of trace elements within a short time once the calibration function for the system is established.

  The results for grass samples from different regions show, that noun specific altitude dependence is present. The regions near human objects like Maljowitza hotels and Moussala station collect more Fe contents, probably due to the metal scrap from building construction.