

In-Situ Analysis of Traces, Minor and Major Elements in Rocks and Soils with a Portable XRF Spectrometer*

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Abstract

The portable rugged EDXRF analyzer SPECTROSCOUT, in combination with an optimized Geo hardware and application package, provides precise and accurate analytical results for traces, minor and major elements in ores, rocks, sediments, soils and sludge prepared as dried powder in disposable XRF sample cups. The SPECTROSCOUT in this version is equipped with a sample spinner and a small vacuum pump to analyze all elements of interest from sodium to uranium in-situ.

Determining elemental compositions for mining and geological use presents substantial challenges. Field conditions can vary widely. Geological field explorations all share a common set of analytical requirements. The need to deliver onsite analytical results is a primary concern. Sending samples back to the laboratory adds significant time delays to most projects. In fact, it may render some tasks impractical or impossible. Real-time analytical results are essential for assessing progress and for making data-based changes to the direction of drilling. Accuracy is also a necessity. Users require dependable accuracy at all detection levels, from trace elements to high-percentage concentrations.

Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry provides a convenient, rapid method of analysis for geochemical exploration and environmental monitoring. Usually, only little sample preparation is required for XRF. Although for many applications the samples are prepared as pressed powder pellets and analyzed in the lab, EDXRF in combination with a sample preparation of dried powder in XRF sample cups can satisfy the needs for precision and detection limits for onsite analysis.

Instrumentation - SPECTROSCOUT

For optimized excitation of the elements in the sample, the spectrometer is equipped with a 10 W transmission X-ray tube in combination with a filter changer. The integrated sample spinner supports the analysis of a large area of the sample surface; a CCD camera enables the positioning when observing smaller sample areas. To be able to analyze “light” elements, the instrument operates under vacuum conditions. The fluorescence radiation is collected using a high-resolution large area SDD. The resolution of the SDD used is <155 eV (Mn K α) at an input count rate of up to 200,000 cps. The components are packaged in a small cabinet with a footprint of 31 cm x 31 cm and a transport height of 27

cm; the weight is only 12 kg, which enables easy carrying of the instrument onsite. The measurement parameters are given in [Table 1](#). Particle size effects were reduced by applying a steep take off angle of 60° and steep angle of incidence of 75°. Before measurement of each spectrum of an unknown sample, the instrument shutter is irradiated to calculate the line energy-channel position function and the line width-line energy relation to correct for any potential drift of the spectrometer.

Sample Preparation

International standard reference samples were used for this report. For the analysis of unknown samples, the material has to be crushed and ground to achieve an average particle size of < 60 µm and then dried. Approx. 10.6 g of the dried powder was filled into a plastic cup with an outer diameter of 40 mm, and then closed with a 4 µm thick polypropylene foil. The cups were rotated during measurement.

Calibration

Calibration for major, minor and trace elements was performed by measuring a series of international reference materials from various sources like: NIST, IRMM, USGS, CRPG, GBW, AMIS, SARM, and others.

The mass absorption coefficient for the Compton scattered Rh K-line was calibrated using the Compton intensity ([Figure 1](#)). The calibration shows a correlation coefficient of 0.9997. Absorption and enhancement effects within the sample are calculated based on a fundamental parameter approach. The matrix effect of the nondetectable compounds, like carbon compounds (e.g., coal, sludge), CO₂ (e.g., from limestone and dolomite), H₂O (crystal water) was calculated applying the calibrated mass absorption coefficient of the Compton scattered Rh K-line. Limitations of classical Compton methods (Andermann and Kemp, 1958) caused by absorption edges between fluorescence lines and Compton lines are corrected automatically by the fundamental parameter model. Some of the listed standard reference materials were used to calibrate slope, intercept and line overlap corrections. The analytes within the atomic number range of Z = 27...92 are calibrated using a Compton model (Andermann and Kemp, 1958) in the concentration range < 8000 µg/g. If one of these elements has a concentration higher than 8000 µg/g, the fundamental parameter based model described is automatically used. A summary of the calibration data is given in [Table 2](#). Correlations for the elements Cr, Th and Ba are shown in [Figure 2](#), [Figure 3](#), and [Figure 4](#). This method allows the analysis of oxidic as well as sulfidic samples using the same calibration.

A pure quartz sample was measured 10 times to determine the lower limits of detection, LOD. The absolute standard deviation of the counts within the element specific ROIs (1,1*FWHM) of the quartz sample spectra and sensitivities was used to calculate the LOD values of [Table 2](#) using the following equation.

$$LOD = \frac{3 * ASD}{t_L * S}$$

where LOD = Limit of Detection, ASD = Absolute standard deviation of the counts in a region of interest (1,1* FWHM) of an element specific line i at ten repeat measurements of a pure quartz sample, t_L = Live time in s and S = Sensitivity in cps/($\mu\text{g/g}$).

Instead of using a pure quartz sample, a suitable standard can be used to calculate the limits of detection. The concentration of an observed element should be 10 times higher than the detection limit when using the following equation:

$$LOD = 3 * C_0 \frac{\sqrt{B}}{N}$$

where LOD = Limit of Detection, N = Counts of an element specific line of a standard within a ROI having a width of 1,1*FWHM, B = Background behind the line within the same ROI and C_0 = Concentration of the observed element in the standard.

The full width of the half maximum (FWHM) is calculated from the Gaussian width-over-energy calibration. Both methods (Eqn 1 and 2) of calculating the limit of detection, LOD, show similar values. Matrix effects and line overlaps might increase the detection limits given in [Table 2](#) significantly (e.g., Co traces in Iron rich samples).

Analytical Performance

The excellent performance of the SPECTROSCOUT can be shown in this multi-element application. Analytical results for three different reference materials are given in comparison to the certified values in [Table 3](#) (GSP-2), [Table 4](#) (GSS-8) and [Table 5](#) (AGV-2). The accuracy of the calculated concentrations for the “light” elements Na, Mg, Al, Si, P, and S is limited by particle size effects caused by differences in the applied sample preparation technology of the different producers and by mineralogical effects.

Repeatability

The repeatability of the SPECTROSCOUT was tested by analyzing the geological reference material AC-E. The standard was measured 14 times during one day. [Table 6](#) shows the average concentrations, the absolute standard deviation, ASD, the relative standard deviation, RSD, of the repeats as well as the comparison between the average concentration values and the certified concentrations. The data demonstrate the excellent precision of the SPECTROSCOUT.

Conclusion

The SPECTROSCOUT simultaneous XRF spectrometer provides a fast, precise, accurate and economic solution for in-situ analysis of traces, minor and major elements in rocks and soils prepared as loose dried powder in plastic cups.

References Cited

Andermann, G., and J.W. Kemp, 1958, Scattered X-Rays as Internal Standards in X-Ray Emission spectroscopy: *Analytical Chemistry*, V. 30/8, p. 1306-1309.

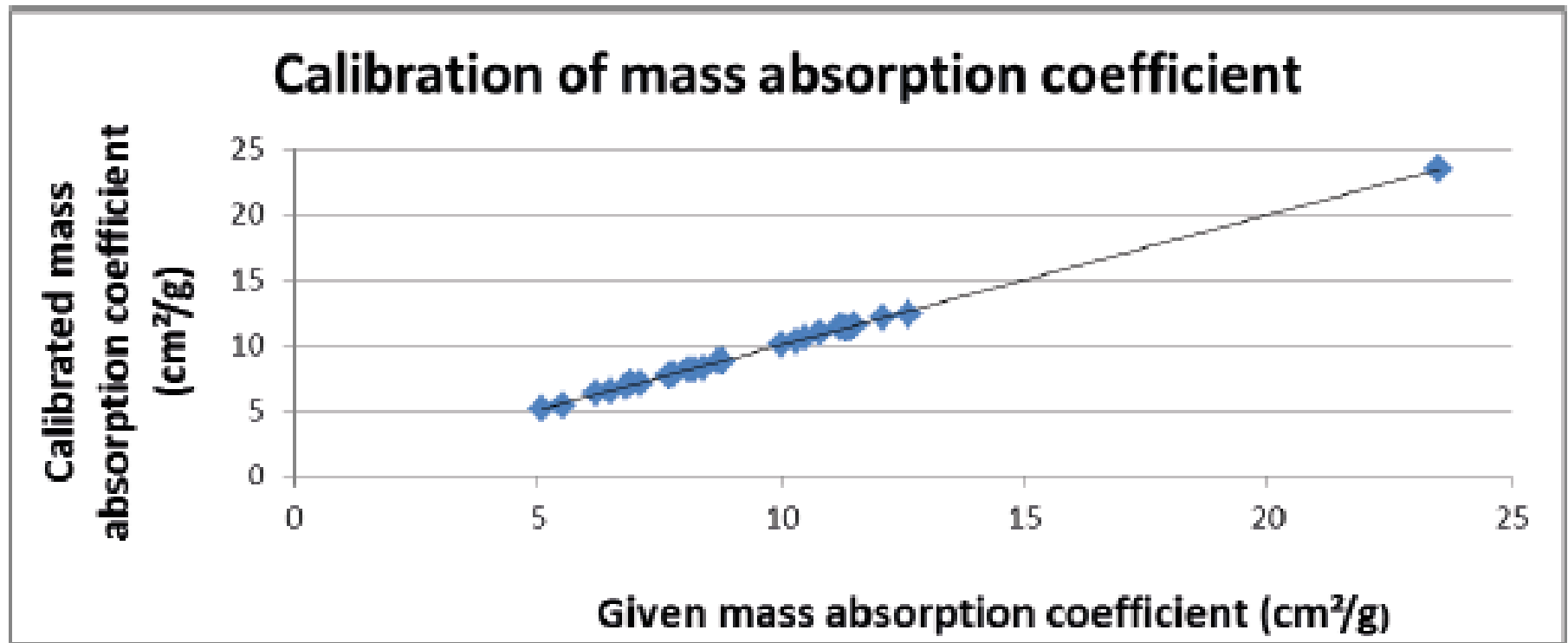


Figure 1. Calibrated mass absorption coefficient for Compton scattered Rh K-line that expected based on sample composition.

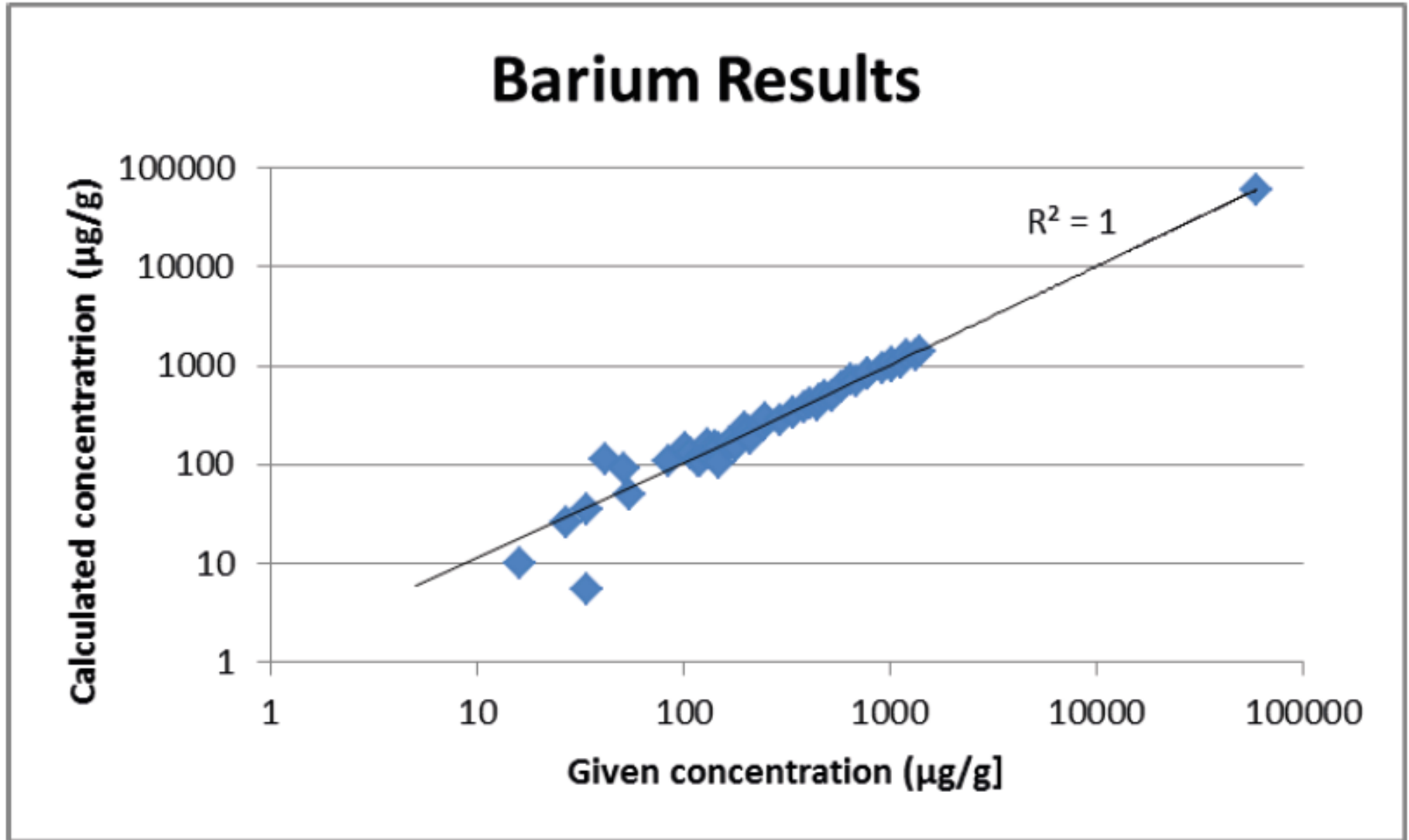


Figure 2. Comparison (log scale) between analyzed Barium concentrations and given values (correlation coefficient: 0,99999).

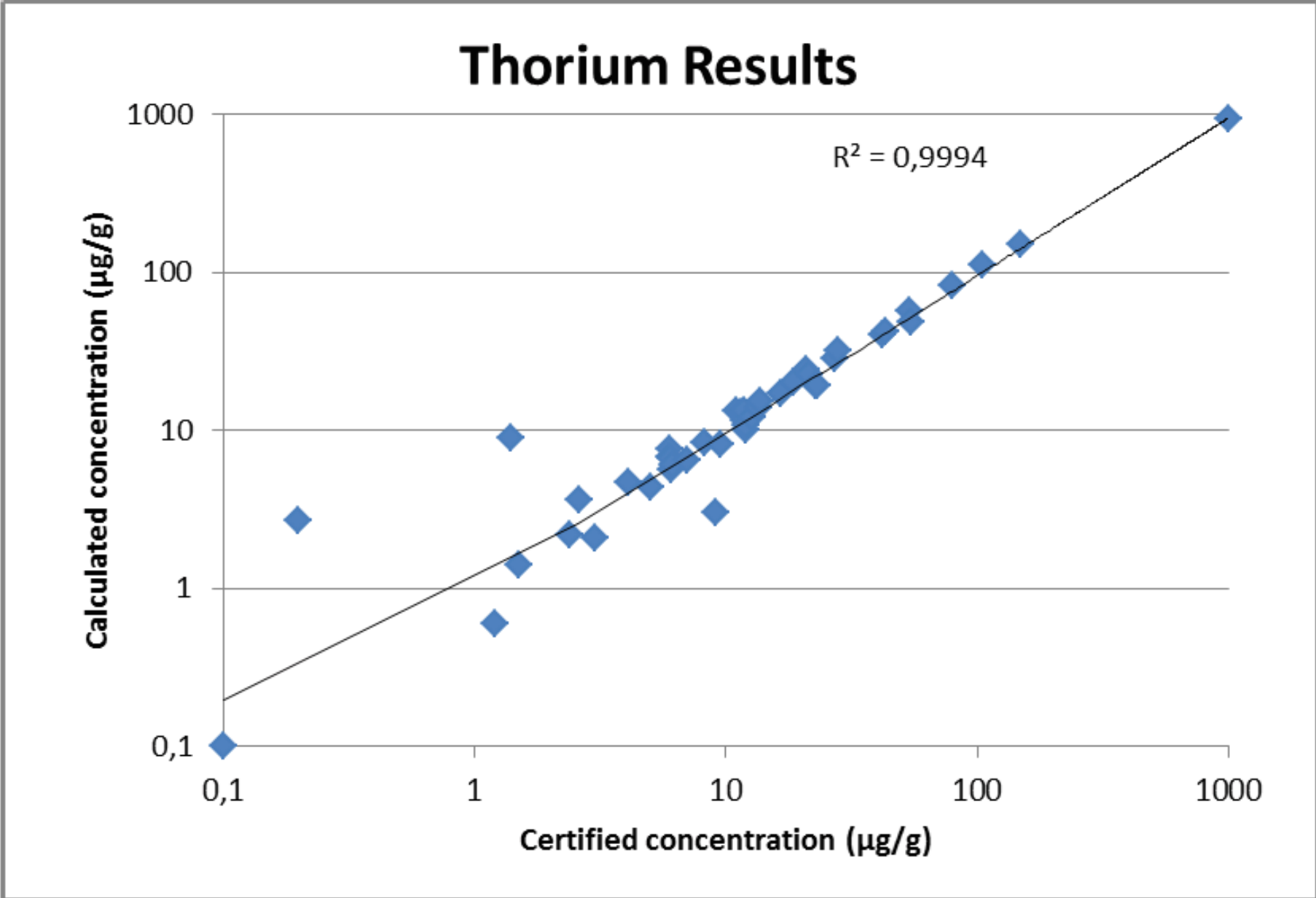


Figure 3. Comparison (log scale) between analyzed Thorium concentrations and given values.

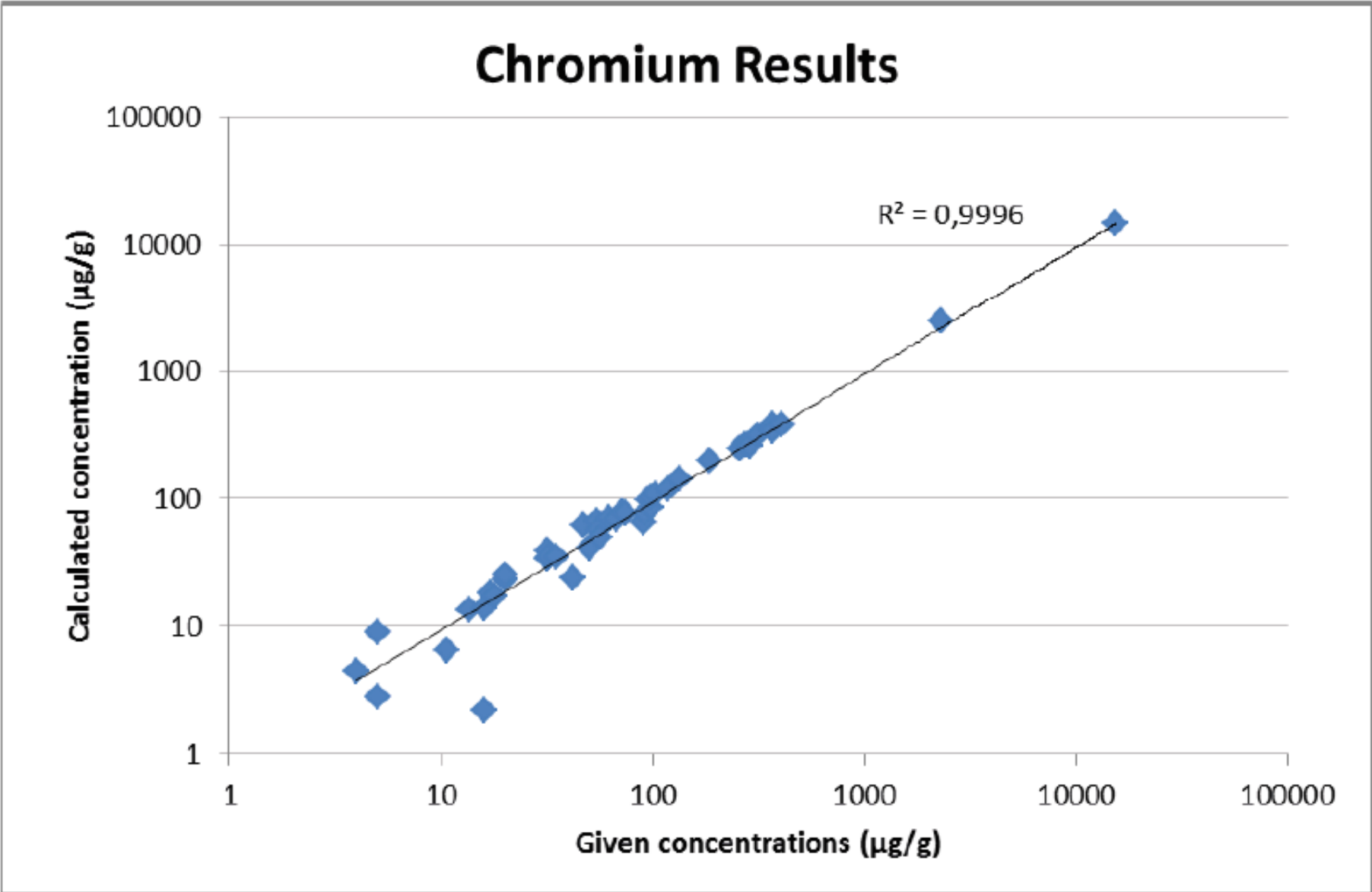


Figure 4. Comparison (log scale) between analyzed Chromium concentrations and given values.

Elements	Tube Anode	Tube Voltage [kV]	Meas. Time [s]
Na - Cl	Rh	11	150
K - Zn, Hf - W	Rh	35	150
Ga - Ce, Hg - U	Rh	50	500

Table 1. Measurement Conditions.

Element/ Oxide	LOD in SiO ₂ [μg/g]	Calibrated concentration ranges [μg/g]	Element/ Oxide	LOD in SiO ₂ [μg/g]	Calibrated concentration ranges [μg/g]
Na ₂ O	400	< 105,000	Br	0.2	< 30
MgO	200	< 500,000	Rb	0.15	< 8,500
Al ₂ O ₃	100	< 600,000	Sr	0.2	< 50,000
SiO ₂		< 1,000,000	Y	0.2	< 700
P ₂ O ₅	20	< 350,000	Zr	0.4	< 1,500
S	10	< 250,000	Nb	0.6	< 300
Cl	30	< 800	Mo	0.8	< 2,500
K ₂ O	25	< 130,000	Sn	2	< 1,300
CaO	20	< 500,000	Sb	1	< 100
Ti	8	< 20,000	Cs	4	< 600
V	5	< 450	Ba	6	< 60,000
Cr	3	< 15,000	La	10	< 30,000
Mn	2	< 9,000	Ce	12	< 40,000
Fe ₂ O ₃	3	< 550,000	Hf	3	< 30
Co	1.2	< 120	Ta	2	< 300
Ni	0.7	< 4,000	W	0.9	< 500
Cu	0.6	< 5,000	Hg	1.3	< 10
Zn	0.4	< 3,000	Tl	0.5	< 30
Ga	0.8	< 100	Pb*	0.5	< 600
Ge	0.7	< 10	Bi	0.5	< 50
As	0.4	< 400	Th	0.3	< 1,000
Se	0.2	< 20	U	0.4	< 650

Table 2. Calibrated concentration ranges and limits of detection (3 sigma).

Element/ Oxide	Unit	Measured	Certified
Na ₂ O	%	2.6 ± 0.1	2.78
MgO	%	1.36 ± 0.04	0.962
Al ₂ O ₃	%	13.6 ± 0.04	14.9
SiO ₂	%	66.3 ± 0.1	66.6
P ₂ O ₅	%	0.28 ± 0.01	0.298
K ₂ O	%	5.25 ± 0.04	5.4
CaO	%	2.08 ± 0.04	2.1
Ti	μg/g	3,969 ± 46	4,000
V	μg/g	52 ± 12	52
Cr	μg/g	27 ± 2	20
MnO	μg/g	417 ± 8	413
Fe ₂ O ₃	%	4.76 ± 0.02	4.9
Co	μg/g	< 16	7.3
Ni	μg/g	15 ± 1	17
Cu	μg/g	39 ± 1	43
Zn	μg/g	116 ± 2	120
Ga	μg/g	19 ± 1	22
Rb	μg/g	242 ± 1	245
Sr	μg/g	248 ± 1	240
Y	μg/g	28.8 ± 0.6	28
Zr	μg/g	545 ± 1	550
Nb	μg/g	27.6 ± 0,4	27
Mo	μg/g	< 0.6	2.1
Cs	μg/g	< 5	1.2
Ba	μg/g	1,278 ± 8	1,340
La	μg/g	155 ± 10	180
Ce	μg/g	343 ± 10	410
Hf	μg/g	9 ± 1	14
Ta		9.6 ± 1.1	
Tl	μg/g	1.7 ± 0.4	1.1
Pb	μg/g	47 ± 1	42
Th	μg/g	112 ± 1	105
U	μg/g	2.8 ± 1	2.4

Table 3. Analytical results including counting statistical error.

Element/ Oxide	Unit	Measured	Certified	Element/ Oxide	Unit	Measured	Certified
Na ₂ O	%	0.9 ± 0.1	1.72	Br	µg/g	1.9 ± 0.2	2.6
MgO	%	3.35 ± 0.05	2.38	Rb	µg/g	93.2 < 0.6	96
Al ₂ O ₃	%	11.72 ± 0.04	11.91	Sr	µg/g	231 < 1	236
SiO ₂	%	51.3 ± 0.1	58.61	Y	µg/g	27.7 ± 0.4	26
P ₂ O ₅	%	0.167 ± 0.004	0.18	Zr	µg/g	217.4 ± 0.8	229
S	%	0.02 ± 0.001	0.012	Nb	µg/g	11,5 ± 0.4	15
Cl	%	0.014 ± 0.001	0.007	Mo	µg/g	< 1	1.2
K ₂ O	%	2.33 ± 0.02	2.42	Sn	µg/g	< 2	2.8
CaO	%	8.50 ± 0.03	8.27	Sb	µg/g	< 1	1
Ti	µg/g	3,662 ± 40	3,837	Cs	µg/g	< 5	7.5
V	µg/g	75 ± 11	81.4	Ba	µg/g	489 ± 7	480
Cr	µg/g	69 ± 4	68	La	µg/g	21 ± 8	35.5
MnO	µg/g	809 ± 11	800	Ce	µg/g	46 ± 7	66
Fe ₂ O ₃	%	4.31 ± 0.01	4.48	Ta	µg/g	6.2 ± 1	1.1
Co	µg/g	< 15	12.7	W	µg/g	< 1.3	1.7
Ni	µg/g	33 ± 1	31.5	Tl	µg/g	< 0.6	0.6
Cu	µg/g	22 ± 1	24,3	Pb	µg/g	21.1 ± 0.8	21
Zn	µg/g	61 ± 1	68	Bi	µg/g	0.6 ± 0.4	0.3
Ga	µg/g	11 ± 1	14.8	Th	µg/g	11.8 ± 0.6	11.8
Ge	µg/g	< 0.9	1.3	U	µg/g	3.3 ± 0.8	2.7
As	µg/g	12.5 ± 0.6	12.7				

Table 4. Analytical results including counting statistical error.

Element/ Oxide	Unit	Measured	Certified	Element/ Oxide	Unit	Measured	Certified
Na ₂ O	%	3.9 +/- 0.2	4.19	Rb	μg/g	67 +/- 0.6	68.6
MgO	%	1.69 +/- 0.04	1.79	Sr	μg/g	652 +/- 1	658
Al ₂ O ₃	%	14.9 +/- 0.1	16.91	Y	μg/g	21.6 +/- 0,4	20
SiO ₂	%	58.8 +/- 0.1	59.3	Zr	μg/g	222 +/- 1	230
P ₂ O ₅	%	0.470 +/- 0.006	0.48	Nb	μg/g	12 +/- 0.4	15
K ₂ O	%	2.74 +/- 0.02	2.88	Sn	μg/g	5.9 +/- 0.6	2.3
CaO	%	4.97 +/- 0.03	5.2	Sb	μg/g	< 1.1	0.6
Ti	μg/g	6,240 +/- 60	6,294	Cs	μg/g	< 5.3	1.2
V	μg/g	120 +/- 14	120	Ba	μg/g	1,082 +/- 8	1,140
Cr	μg/g	18 +/- 2	17	La	μg/g	24 +/- 9	38
MnO	μg/g	963 +/- 12	994.2	Ce	μg/g	44 +/- 7	68
Fe ₂ O ₃	%	6.39 +/- 0.01	6.69	Hf	μg/g	3.5 +/- 0.6	5.1
Co	μg/g	< 20	16	Ta	μg/g	8 +/- 2	0.9
Ni	μg/g	21 +/- 1	19	Tl	μg/g	< 0.7	0.3
Cu	μg/g	52 +/- 2	53	Pb	μg/g	15 +/- 1	13
Zn	μg/g	81 +/- 1	86	Th	μg/g	6.7 +/- 0.4	6.1
Ga	μg/g	18 +/- 1	20	U	μg/g	2.7 +/- 0.8	1.9

Table 5. Analytical results including counting statistical error.

Element/ Oxide	Unit	Average	ASD (1s)	RSD (1s)	Certified
Na ₂ O	%	6.20 +/- 0.06	1.0	6.54	
MgO	%	0.04 +/- 0.01	25.0	0.03	
Al ₂ O ₃	%	12.80 +/- 0.05	0.4	14.7	
SiO ₂	%	67.80 +/- 0.2	0.3	70.35	
P ₂ O ₅	%	0.02 +/- 0.003	2.5	0.014	
K ₂ O	%	4.29 +/- 0.03	0.6	4.49	
CaO	%	0.38 +/- 0.01	3.0	0.34	
Ti	μg/g	500 +/- 23.4	4.7	659	
V	μg/g	11 +/- 3.3	29.0	3.3	
MnO	μg/g	583 +/- 8.1	1.4	580	
Fe ₂ O ₃	%	2.46 +/- 0.03	1.1	2.53	
Ni	μg/g	4 +/- 0.6	14.0	1.5	
Cu	μg/g	2 +/- 0.6	26.0	4	
Zn	μg/g	210 +/- 1.5	0.7	224	
Ga	μg/g	40.0 +/- 0.5	1.3	39	
Br	μg/g	0.7 +/- 0.1	17.0	0.5	
Rb	μg/g	149 +/- 1.4	0.9	152	
Sr	μg/g	3.8 +/- 0.1	3.7	3	
Y	μg/g	198 +/- 1.3	0.7	184	
Zr	μg/g	834 +/- 6.5	0.8	780	
Nb	μg/g	114 +/- 0.7	0.6	110	
Sn	μg/g	8 +/- 2.4	30.0	13	
Ba	μg/g	59 +/- 4.9	8.3	55	
La	μg/g	75 +/- 5.2	6.9	59	
Ce	μg/g	213 +/- 7.8	3.7	154	
Hf	μg/g	21 +/- 0.6	2.8	28	
Ta	μg/g	9 +/- 2.0	23.0	6	
W	μg/g	5 +/- 1.3	26.0	1.5	
Tl	μg/g	0.7 +/- 0.1	13.0	0.9	
Pb	μg/g	42.1 +/- 0.5	1.1	39	
Th	μg/g	20.9 +/- 0.3	1.7	18.5	
U	μg/g	5.6 +/- 0.3	5.8	4.6	

Table 6. Results of a reproducibility test with geological reference material AC-E.