GEOLOGIJA. 2011. Vol. 53. No. 2(74). P. 69–74

Comparison of two analytical methods for the chemical characterization of flint from Lithuania and Belarus

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Hughes R. E., Baltrūnas V., Kulbickas D. Comparison of two analytical methods for the chemical characterization of flint from Lithuania and Belarus. *Geologija*. Vilnius. 2011. Vol. 53. No. 2(74). P. 69–74. ISSN 1392-110X.

In this paper, authors present the results of interlaboratory comparison of two different methods of determining the chemical composition of Lithuanian and Belarusian flint: direct current arc emission spectrophotometry (DCAES) and energy dispersive X-ray fluorescence (EDXRF). For this interlaboratory comparison, geological specimens from three Lithuanian and Belarusian flint sources, previously analysed by Baltrūnas et al. (2006a), were sent to the first author for a non-destructive EDXRF analysis. All three sources were important for prehistoric tool manufacturing during Lithuanian prehistory. Non-destructive EDXRF analyses of flint may be preferred in situations where it is important to conserve archaeological artifacts, whereas DCAES is capable of analyzing more elements with precision which may be needed to identify flint with overlapping Ca / Fe compositions that cannot be separated by non-destructive EDXRF. The interlaboratory comparison results we present here illustrate the importance of international cooperation among geoscientists and archaeologists interested in applying chemical and geological methods and data to study the economic, social and cultural processes operating during different times in the prehistoric past.

Key words: flint, geochemistry, energy dispersive X-ray fluorescence (EDXRF) analysis, Lithuania, Belarus

Received 29 April 2011, accepted 12 June 2011

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INTRODUCTION

Baltrūnas et al. (2006 a, b) have recently published important articles on the chemistry and archaeological significance of flint in prehistoric Lithuania. These studies, especially of Baltrūnas et al. (2006a), provide baseline data on the chemical composition of several archaeologically significant Lithuanian flints that will be important in future geoarchaeological research in the region. Hughes et al. (2010) conducted a pilot study of Scandinavian flint, with the same general aims as those of Baltrūnas and colleagues, to determine the chemical "signatures" of different varieties of flint, to trace their geographic dispersals, and to apply these chemical and spatial distinctions to the study of the trade, exchange, and conveyance of these materials in prehistory (Baltrūnas et al., 2007).

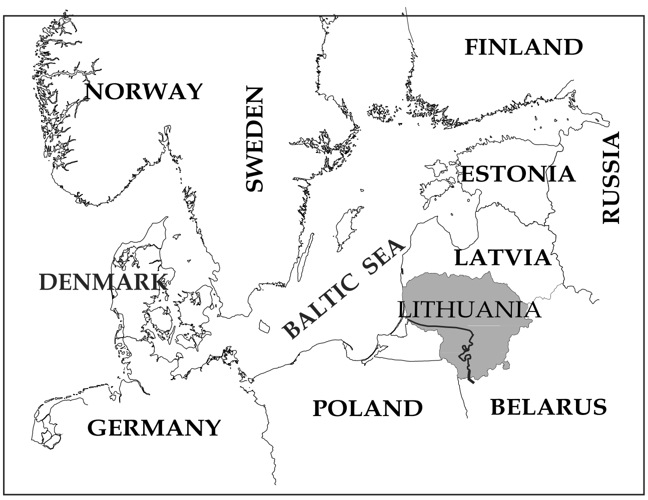
In this paper, we present the results of interlaboratory comparison of two different methods of determining the chemical composition of Lithuanian and Belarusian flint – direct current arc emission spectrophotometry (DCAES) and energy dispersive X-ray fluorescence (EDXRF). Because each method possesses different advantages, we undertook complementary analyses of the same source specimens to be able to evaluate and compare how each method might serve archaeological ends under different circumstances. We begin by pointing out differences between these two approaches. Perhaps the most important one, from the archaeological standpoint, is that to determine the quantitative composition, DCAES requires that the sample be vaporized to generate a plasma which emits the visible light that can then be analyzed to determine the composition. Hence, it requires sacrificing some portion of a sample (geological or archaeological) for analysis. EDXRF, as employed here, is completely non-destructive as no portion of geological or archaeological samples is altered. On the other hand, DCAES has much lower detection limits (MDL) for certain elements than does non-destructive EDXRF (see below) and is, therefore, capable of measuring many more chemical elements with a greater precision.

ANALYTICAL CONDITIONS

Baltrūnas et al. (2006a: 14–16) report the details of analytical conditions used for DCAES determination of the composition of 28 elements in several Lithuanian flints and artifacts. For this interlaboratory comparison, geological specimens from three Lithuanian flint sources, previously analyzed by Baltrūnas et al. (2006a), were sent to the first author for a non-destructive EDXRF analysis. The source specimens were from the Grodno (Grandichi) chalk quarry in Belarus, the Margionys quarry in southern Lithuania, and from Nemunėlio Radviliškis in northern Lithuania (Baltrūnas et al., 2006a) (Fig. 1). All three sources were important for prehistoric tool manufacturing during Lithuanian prehistory (Makhnach, Gulis, 1993; Karabanov, 1997; Baltrūnas et al., 2006b).

Margionys is located in the sandy South-Eastern (Dainava) Plain which is made up of glaciofluvial sediments consisting of badly sorted gravel with coarse pebbles and boulders containing numerous flint concretions and debris. *In situ* carbonaceous Cretaceous sediments are exposed only further south of Margionys in the Grodno district of Belarus. One of the Upper Cretaceous flint concretions 10–30 cm in diameter from the Grandichi (Grodno district in Belarus) chalk quarry south of Lithuania was taken for comparison. Neolithic and Bronze Age flint mines are known in the western part of the Grodno region. Upper Devonian layers of the Įstras Formation outcrop in north Lithuania near the Nemunėlio Radviliškis township, where siliceous nodules up to 20–30 cm in diameter occur in the dolomite powder interlayers.

EDXRF analysis of five specimens from each source was conducted using a QuanX-EC™ (Thermo Electron Corporation) EDXRF spectrometer equipped with a silver (Ag) transmission target X-ray tube, a 50 kV X-ray generator, a digital pulse processor with automated energy calibration, and a Peltier cooled solid state detector with 145 eV resolution (FWHM) at 5.9 keV. The X-ray tube was operated at differing voltage and current settings to optimize excitation of the elements selected for analysis. Sample pretreatment for the whole rock EDXRF analysis was limited to cleaning their surface with distilled water to remove any noticeable surface contaminants. Special care was taken to avoid directing the X-ray beam onto obvious patinated surfaces and calcareous and fossil inclusions. The only other requirement was that each sample be relatively flat, >ca. 2–3 mm thick, and >15–20 mm in diameter.



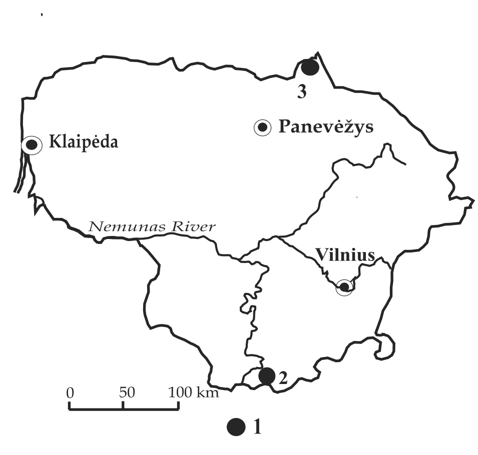


Fig. 1. Locations of flint sources: *1* – Grodno (Grandichi) (53°23′06″N, 23°47′03″E), *2* – Margionys (54°00′03″N, 24°17′32″E), *3* – Nemunėlio Radviliškis (56°23′59″N, 24°46′24″E)

1 pav. Titnagų tyrimo vietos: *1* – Gardinas (53°23′06″N, 23°47′03″E), *2* – Margionys (54°00′03″N, 24°17′32″E), *3* – Nemunėlio Radviliškis (56°23′59″N, 24°46′24″E)

Previous analysis (Hughes et al., 2010) showed that X-ray intensities above background for certain trace elements in flint were too low to yield reliable composition estimates, so analyses here focused on nine major and selected minor elements. Intensities for Al, Si, S, Cl, K, Ca, Ti, Mn and Fe (using the Kα emission line for each element) typically yielded adequate count rates (counts / second over background), although Table 1 shows that the coefficients of variation (CV %) for some elements were more variable than others because of the low concentrations approach detection limits. Si, Ca, and Fe yielded the highest count rates (counts / second over background), total counts, and the most stable composition estimates, so these elements were employed to explore differences among Lithuanian flint sources. The analyses for SiO_2, CaO, and $Fe_2O_3^T$ were conducted at 300 deadtime-corrected seconds in vacuum to generate background subtracted integrated net count rate (counts / second) data, which were converted to composition estimates (ppm and weight percent composition) after overlapping Kα, and Kβ line contribution from adjacent elements was stripped and matrix correction algorithms applied. The X-ray tube current was scaled automatically to the physical size of each specimen. Because of the extremely high SiO_2

Table 1. **Quantitative composition estimates for geological samples of flint from Lithuania and Belarus, determined by energy dispersive X-ray fluorescence (EDXRF)***

1 lentelė. **Lietuvos ir Baltarusijos titnagų sudėtis, nustatyta energijos dispersijos X spindulių fluorescencijos metodu**

	Geologic source samples			Geostandard	
	Grandichi (n = 5)	Margionys (n = 5)	Nemunėlio Radviliškis (n = 5)	JCh-1 (measured) (n = 10)	JCh-1 (recommended)
			Al_2O_3 (wt.%)		
Mean	0.146	0.082	0.091	0.825	0.734
S. D.	0.03	0.019	0.089	0.018	
CV%	20.6	23.3	114.8	2.2	
			SiO_2 (wt.%)		
Mean	99.43	99.47	88.73	98.25	97.81
S. D.	0.154	0.036	5.69	0.081	
CV%	1.6	1.9	6.4	0.001	
			SO_3 (wt.%)		
Mean	0.026	0.024	0.047	0.005	4
S. D.	0.005	0.004	0.003	0.001	
CV%	18.1	15.8	7.2	21.9	
			Cl (ppm)		
Mean	116	39	828	0	14
S. D.	28.58	33.94	177.9		
CV%	24.63	87	21.5		
			K_2O (wt.%)		
Mean	0.045	0.043	0.0025	0.219	0.221
S. D.	0.003	0.003	0.043	0.011	
CV%	5.7	7.1	114.1	5	
			CaO (wt.%)		
Mean	0.189	0.049	9.93	0.039	0.045
S. D.	0.055	0.01	1.04	0.001	
CV%	28.8	21.2	10.43	3.1	
			Ti (ppm)		
Mean	41.4	24	107.4	191.7	189
S. D.	9.56	5.15	14.12	13.67	
CV%	23.1	21.5	13.15	7.1	
			Mn (ppm)		
Mean	1	1.8	58	139.9	134
S. D.	1.4	1.79	37.47	4.15	
CV%	141.4	99.4	64.6	3	
			$Fe_2O_3^T$ (ppm)		
Mean	204	187.6	663.6	3781.8	3560
S. D.	25.33	38.33	127.75	13.46	
CV%	12.4	20.4	19.25	3.6	

* Five samples analyzed from each source. EDXRF-measured summary statistics for JCh-1 pooled from 10 analyses. Recommended values for JCh-1 from Imai et al. (1996). SO_3 value recommended for JCh-1 in ppm, not %. S. D. = standard deviation; CV% = coefficient of variation.

composition of flint, the Geological Survey of Japan's JCh-1 chert standard was analyzed with each run of geological samples to monitor machine precision and accuracy (see Table 1). Minimum detection limits (MDL) for elements measured by EDXRF in Table 1 were determined to be: Al_2O_3 – .044%; SiO_2 – .009%; SO_3 – .001%; Cl – 11 ppm; K_2O – .003%; CaO – .003%; Ti – 13 ppm; Mn – 3 ppm; $Fe_2O_3^T$ – 3 ppm.

Several factors influence the evaluation of the precision and accuracy of non-destructive EDXRF analysis. These are discussed in Hughes et al. (n. d.) and involve: 1) the homogeneity or heterogeneity of the material being measured, 2) the physical surface to be analyzed, 3) caveats associated with the bulk area, near-surface techniques, and 4) effects of patination and other surface adherents on the derived composition estimates. In addition to sample surface irregularities, some Lithuanian flint samples (particularly those from Nemunėlio Radviliškis) displayed many inclusions and Ca-rich areas (see Baltrūnas et al., 2006a: Fig. 4) that were nearly impossible to avoid via EDXRF analysis, even using a small (3.5 mm) X-ray aperture. Although every effort was made to focus the X-ray beam exclusively on areas lacking such obvious spots, the high variability in EDXRF summary statistics for Nemunėlio Radviliškis (see Table 1) undoubtedly reflected the contribution from heterogeneous portions of the samples, which could not be eliminated from X-ray excitation and quantification.

The decision to analyze samples non-destructively by EDXRF was made mainly to serve archaeological ends. However, conducting only EDXRF analyses which do not alter the physical shape of an artifact in any way made it mandatory for comparative purposes that the same general analytical "noise" introduced by sample shape irregularities in archaeological artifacts should be present also in geological reference samples. Hence, it is important to analyze geological samples as-is so that one may compare like with like. Even though shape irregularities contribute significantly to the scatter observed for certain elements (see Table 1 and Figs. 1 and 2), they provide a more faithful representation of "real world" variability than repeated analyses of a single spot used to assess machine precision (Table 1).

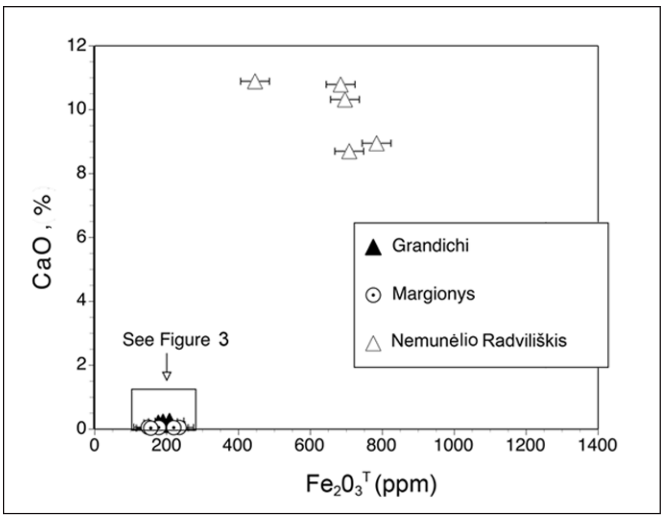


Fig. 2. CaO vs. $Fe_20_3^T$ composition of archaeologically significant flint from Lithuania and Belarus, determined by EDXRF

Caption: Error bars are 2 σ error estimates for each sample. CaO error estimates do not show at this scale. Five specimens were analyzed from each locality.

2 pav. Archeologiniu požiūriu vertingų titnagų iš Lietuvos ir Baltarusijos CaO *vs*. $Fe_20_3^T$ sudėtis, nustatyta EDXRF metodu

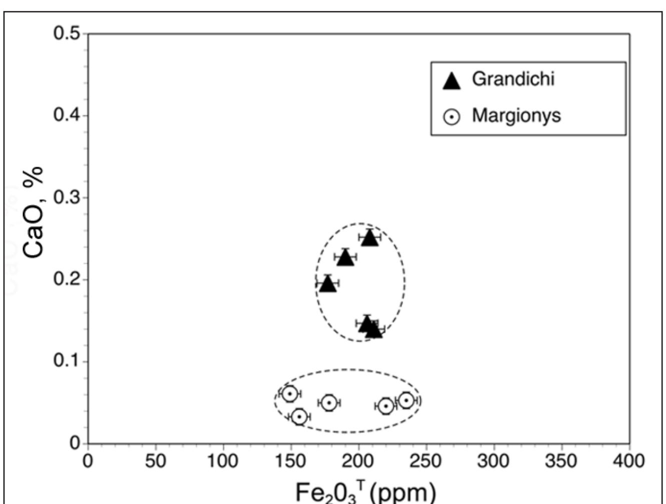


Fig. 3. CaO vs. $Fe_20_3^T$ composition of flint from Grandichi (Grodno, Belarus) and Margionys (Lithuania), determined by EDXRF

Caption: Error bars are 2 σ error estimates for each sample. CaO error estimates do not show at this scale. Five specimens were analyzed from each locality.

3 pav. Titnagų iš Gardino ir Margionių CaO *vs*. $Fe_20_3^T$ sudėtis, nustatyta EDXRF metodu

RESULTS AND DISCUSSION

Table 2 presents data on four elements measured in common (Ca, Fe, Mn, and Ti) by DCAS and EDXRF for each of the three flint sources. As noted above, DCAES analysis generated composition estimates for many elements that could not be analyzed with precision by EDXRF, while measurements for Cl, K_2O, SO_3 and SiO_2 were determined by EDXRF but not by DCAES. Table 2 shows a good agreement between techniques for measuring elements from certain sources, while there are differences between them in others. For example, both techniques yielded statistically identical results for Ca composition in Grandichi and Margionys flint, although values for Ti and Mn are variant. For Grandichi and Margionys, the Mn values determined by EDXRF are arithmetic only because they exceed MDL. Fe values for Margionys are significantly greater by DCAES than via EDXRF. From the standpoint of EDXRF analysis, between-technique comparison for specimens from Nemunėlio Radviliškis is problematic. As noted, the extreme heterogeneity of this flint yielded correspondingly variable composition estimates; consequently, the EDXRF values in Tables 1 and 2 should be viewed with caution. Baltrunas et al. (2006a: 18) commented that the "differences among separate parts of concretions and nodules in concentrations of chemical elements are rather pronounced", and this observation was clearly supported by EDXRF data.

As was demonstrated in an earlier study (Baltrunas et al., 2006a), DCAES was able to partition the three analyzed Lithuanian flints into discrete chemical groups, using the correlation coefficients and cluster analysis involving many elements. Here, the EDXRF analysis shows that the same separations can be made, albeit using a smaller number of elements. There are inherent limitations to any two-element partitioning which may be revealed as more flints are analyzed (thus requiring use of additional elements), but in this case EDXRF data (Table 1 and Figs. 1 and 2) show that Grodno (Grandichi) and Margionys are quite distinct from Nemunėlio Radviliškis, and that more subtle chemical contrasts in Ca composition allow a distinction between Grandichi and Margionys flints (Fig. 3).

The results of this experiment are compatible with geological data. Flint from the Grandichi quarry is from an *in situ* layer of chalk, while Margionys flint is not *in situ* but derived from Cretaceous rocks which have undergone significant physical and chemical weathering. Flint from Nemunėlio Radviliškis is from Devonian age dolomite rocks deposited in lagoon-like conditions (Makhnach, Gulis, 1993; Kadūnas et al., 2005). Data of correlation analysis of trace elements allow distinguishing three types of siliceous rocks: 1 – from the Upper Cretaceous in South Lithuania and West Belarus (flint concretions); 2 – from the Upper Cretaceous in West Lithuania (silicified gaize); 3 – Upper Devonian in North Lithuania (siliceous nodules). These data are analyzed in a special article (Baltrūnas et al., 2006a). Distribution patterns of geochemical data show that flints from southern Lithuania and western Belarus are genetically similar, and some differences were found only between separate groups of siliceous samples from Quaternary and Cretaceous layers.

CONCLUSIONS

This comparative study shows that both analytical techniques (DCAES and EDXRF) can be successfully used to characterize flint from Lithuania and Belarus. Non-destructive

Table 2. **Comparison of quantitative composition estimates for flint from Lithuania and Belarus***
2 lentelė. **Lietuvos ir Baltarusijos titnagų nustatytos sudėties palyginimas**

	Grandichi (DCAES)	Grandichi (EDXRF)	Margionys (DCAES)	Margionys (EDXRF)	Nemunėlio Radviliškis (DCAES)	Nemunėlio Radviliškis (EDXRF)
Ca (%)						
Mean	0.06	0.135	0.05	0.049	2.62	7.1
S. D.	0.16	0.039	0.003	0.01	0.631	0.74
CV%	26	28.8	6	21.2	24	10.4
Ti (ppm)						
Mean	97	41.4	45	24	94	107.4
S. D.	14	9.56	3	5.15	15	14.12
CV%	15	23.1	7	21.5	16	13.2
Mn (ppm)						
Mean	66	1	110	1.8	144	58
S. D.	34.3	1.4	8	1.79	9.7	37.47
CV%	52	141.4	8	99.4	7	64.6
Fe (%)						
Mean	0.011	0.014	0.21	0.013	0.15	0.046
S. D.	0.02	0.002	0.08	0.003	0.01	0.008
CV%	21	12.4	38	20.5	9	19.3

*DCAES values from Baltrūnas (2006a: Tables 1 and 2). EDXRF values from Table 1 converted from oxide to elemental to facilitate comparison. CaO converted using the formula: CaO% value $\times$ .715 $\times$ 10^4 = Ca %; $Fe_2O_3^T$ ppm converted using the formula: $Fe_2O_3^T$ ppm value $\times$ .699 = Fe ppm. S. D. = standard deviation; CV% = coefficient of variation

EDXRF analyses of flint may be preferred in situations when it is important to conserve archaeological artifacts, whereas DCAES is capable of analyzing more elements with precision which may be needed to identify flint with overlapping Ca / Fe compositions that cannot be separated by non-destructive EDXRF. More generally, the interlaboratory comparison results we present here illustrate the importance of international cooperation by geoscientists and archaeologists interested in applying chemical and geological methods and data to study the economic, social and cultural processes that operated during different times in the prehistoric past.

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LIETUVOS IR BALTARUSIJOS TITNAGŲ CHEMINIŲ CHARAKTERISTIKŲ, GAUTŲ DVIEM ANALITINIAIS METODAIS, PALYGINIMAS

Santrauka

Straipsnyje pateikiami Lietuvos ir Baltarusijos titnagų cheminės sudėties nustatymo dviem skirtingais metodais – atominės emisijos spektrofotometrine analize (DCAES) ir energijos dispersijos X spindulių fluorescencijos analize (EDXRF) – tarplaboratorinio palyginimo rezultatai. Geologiniai pavyzdžiai iš trijų Lietuvos ir Baltarusijos titnago šaltinių, anksčiau analizuotų V. Baltrūno su kolegomis (Baltrūnas et al., 2006a), buvo nusiųsti Richardui E. Hughes'ui EDXRF analizei. Visi titnago šaltiniai buvo svarbūs priešistorinių dirbinių gamybai Lietuvoje. Titnago EDXRF analizei teikiama pirmenybė, kai svarbu išsaugoti archeologinius eksponatus, tuo tarpu DCAES analize galima nustatyti daugiau elementų didesniu tikslumu, kuris reikalingas identifikuojant titnagą su sutampančia Ca-Fe sudėtimi, kurios neišskiria EDXRF metodas. Tarplaboratorinio palyginimo rezultatai iliustruoja geologijos ir archeologijos mokslų bendradarbiavimo svarbą taikant cheminius ir geologinius metodus, taip pat naudojant duomenis ekonominių, socialinių ir kultūrinių procesų, pasireiškusių skirtingais priešistorės laikotarpiais, tyrinėjimui.

Raktažodžiai: titnagas, geochemija, energijos dispersinė rentgeno fluorescencijos analizė (EDXRF), Lietuva, Baltarusija