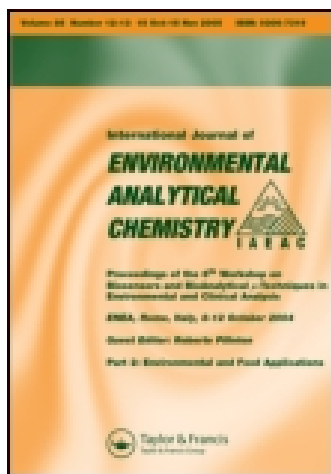


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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/geac20>

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Published online: 04 Apr 2013.

To cite this article: Ralitsa Georgieva, Albena Detcheva, Methody Karadjov, Juri Jordanov & Elisaveta Ivanova (2013) Total reflection X-ray fluorescence analysis of trace elements in Bulgarian bottled mineral waters of low and high mineral content, International Journal of Environmental Analytical Chemistry, 93:10, 1043-1051, DOI: [10.1080/03067319.2013.775277](https://doi.org/10.1080/03067319.2013.775277)

To link to this article: <http://dx.doi.org/10.1080/03067319.2013.775277>

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Total reflection X-ray fluorescence analysis of trace elements in Bulgarian bottled mineral waters of low and high mineral content

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(Received 5 July 2012; final version received 7 January 2013)

The trace elements S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Br, Rb and Ba in Bulgarian bottled mineral waters of low and high total dissolved solids (TDS) content were determined by total reflection X-ray fluorescence (TXRF) analysis using gallium as internal standard. The water samples were analysed after simple preparation consisting in three-fold sequential pipetting/drying of 5 μL portions of the water sample mixed with the internal standard on the quartz holders. The precision of the obtained results is characterised by an RSD of 5–16%. The lower limits of detection (LLDs) in waters of TDS content of 160–420 mg L^{-1} were in the low $\mu\text{g L}^{-1}$ range, whereas those in the water with TDS content of 2900 mg L^{-1} were higher by a factor of 5–15. There is a good agreement between the results for the trace element content obtained by TXRF and inductively coupled plasma optical emission spectrometry (ICP-OES) for mineral waters with TDS content in the range from 160 to 2900 mg L^{-1} .

Keywords: total reflection X-ray fluorescence analysis; Bulgarian bottled mineral waters; trace elements

1. Introduction

Bulgaria is extremely rich in mineral and spring waters. This natural richness has been known and exploited since ancient times, particularly by the Romans (3rd–2nd century BC) who inhabited the Balkan Peninsula and founded numerous sites in the neighbourhood of thermal springs. Even nowadays, however, these natural resources are not sufficiently studied. Owing to particularities of the geological structures, lithology and tectonic movements, the majority of the Bulgarian thermal mineral waters are to be found in the southern and western part of the country [1].

At present, more than 50 brands of bottled mineral, spring and table waters are offered on the Bulgarian market. The major components of bottled Bulgarian waters are monitored in accordance with European legislation, e.g. [2,3], whereas only limited data are available about their trace element content. One publication deals with trace element determination in two brands of bottled Bulgarian mineral waters using wavelength dispersive X-ray fluorescence (WDXRF) analysis after precipitation of the analytes with ammonium pyrrolidine dithiocarbamate [4]. Data on the microelement content of Bulgarian mineral waters at the corresponding sources can be found in [1,5].

The laboratories engaged in quality control of potable waters need rapid, simple and reliable methods for the determination of trace elements. Several methods for trace analysis in potable

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This manuscript was presented at the 37th International Symposium on Environmental Analytical Chemistry (ISEAC-37), Department of Chemistry, University of Antwerp, 22–25 May 2012.

waters are described in national and international regulations [2,3]. Particularly useful are methods providing simultaneous multi-element determination with sufficient sensitivity. Spectrometric techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) are mainly used for the trace element analysis in waters [1,6,7]. WDXRF spectrometry is an excellent method for simultaneous multi-element determination, however, it has seldom been applied to trace element analysis in waters, owing to its insufficient sensitivity [4,8].

In the last two decades total reflection X-ray fluorescence (TXRF) analysis gained popularity as a new technique for determination of both major and trace components in environmental samples [9,10]. The benefits of TXRF include: fast and easy sample preparation; no need of external calibration; multi-element analysis including halogenides; low analytical operation and maintenance costs; portability. TXRF methods for trace element analysis in different kinds of natural waters including mineral waters after separation and preconcentration of the analytes [11–14], as well as direct TXRF methods [6,7,15–21] are reported in the literature.

The purpose of the present work was to study the applicability of the TXRF technique for direct trace element analysis of Bulgarian bottled mineral waters of TDS content in a broad range. Typical representatives of mineral waters of Southern and Western Bulgaria were selected for analysis among Bulgarian natural mineral waters recognised by the EC [22]. The accuracy of the obtained results was checked by analysing the water samples using classical ICP-OES. Informative data about the trace element content of the mineral waters at the corresponding sources were taken from ref. [1].

2. Experimental

2.1 Instrumentation

The TXRF analyser S2 PICOFOX (BRUKER AXS GmbH Karlsruhe, Germany) was used for the measurements. This instrument was equipped with an air-cooled low power X-ray tube (Mo target), a Ni/C monochromator with 80% reflectivity and a liquid nitrogen-free Silicon Drift Detector (SDD) of 10 mm² area with an energy resolution of < 159 eV (Mn K α). The sample holders were quartz optical plates of 30 mm diameter and 3 mm thickness (Perspex Distribution LTD, UK). The power was 50 kV and the current was 1000 μ A. Prior to each series of measurements gain correction was performed to compensate the drift of the channel/energy dependence by measuring at As K α – 10.53 keV.

2.2 Cleaning of the lab ware

The stand with the quartz plates used as sample holders was placed in a 1000 mL beaker containing 10% (v/v) nitric acid (p.a., Merck, Darmstadt, Germany) and was heated at a temperature of 80 °C for 1 h on a hot plate. It was subsequently flushed with tri-distilled water from a quartz apparatus and was let to dry in the air. In the cases when siliconisation of the quartz holder surface was applied, the silicone layer was previously removed with acetone (p.a., Merck). The TXRF analysis of the quartz plates after the cleaning procedure revealed no elevated background or noticeable peaks of trace elements.

2.3 Sample preparation and analysis

Commercial drinking waters of the brands ‘Gorna Bania’, ‘Devin’, ‘Kom’, ‘Thorn Spring’ and ‘Mihalkovo’ bottled in 2011 (bottle volume 0.5 L) were analysed. The ‘Mihalkovo’ water

contains natural free carbon dioxide, which was removed prior to the analysis by ultrasonic treatment [23].

For internal calibration, 1.0 mL of the water was transferred to an Eppendorf® tube of 1.5 mL volume and was mixed with 20 µL of a 10 mg L⁻¹ Ga solution prepared from a Merck titrisol (1000 mg L⁻¹). For the analysis of the low-mineralised waters ('Gorna Bania', 'Devin' 'Kom' and 'Thorn Spring'), the surface of the quartz holders was previously hydrophobised by pipetting 10 µL of a silicone solution in propanol (Serva, Heidelberg, Germany) and subsequent drying for several seconds under IR lamp. Aliquots of 5 µL of the water samples mixed with the internal standard were pipetted on the quartz holder and were dried under IR lamp. Three consecutive pipettings/dryings of each sample solution were performed resulting in a total sample amount of 15 µL. The area of the dry residues obtained as described above, was less than 10 mm² [24]. Three replicates were prepared for each sample. The dry residues were measured for 1000 s and each dry residue was measured twice at two perpendicular positions of the sample holder [17]. Several blank quartz holders were measured as described to determine the blank value.

For the evaluation of the TXRF spectra, the Spectra 5.1® software (Bruker AXS Microanalysis GmbH, Berlin, Germany) was used. The analysis and quantification consisted of the following steps (according to [20]):

- (a) Simultaneous measurement of the whole spectrum.
- (b) All identified elements are marked for further identification by the software.
- (c) Spectral deconvolution by Super Bayes optimisation: on the basis of the chosen elements, the software performs the deconvolution of the spectra. The net intensities of the element peaks are calculated with regard to corrections of line overlaps, background factors, escape peak correction, etc. Deconvolution is assessed according to the χ^2 criterion ($\chi^2 < 10$).
- (d) Calculation of element concentrations by the formula $C_i = [N_i/S_i][N_{is}/S_{is}]^{-1} C_{is}$,

where N is the net intensity, S is the relative sensitivity and C is the concentration – each either of the analyte (i) or the internal standard (is), as indicated. The sensitivity for each analyte is defined as a database in the software. This database can be corrected in case of a drift by measuring a sample containing 1 ng of nickel, as recommended by the manufacturer [24].

The lower limit of detection (LLD_i) for each analyte (i) was determined in each spectrum by the formula: $LLD_i = 3 C_i N_i^{-1} (N_{bg})^{-2}$, where C_i is the concentration, N_i is the area of the fluorescence peak in cps and N_{bg} is the background area subjacent the peak in cps [24]. Then the dependence of LLD on the exposition T is: $LLD \sim 1/T^2$. Formally, the internal standard is not included in the formula for the LLD. However, its sensitivity and concentration participate indirectly in the formula, as they are used for calculating the analyte concentration.

ICP-OES analysis was performed under conventional conditions after preconcentrating the waters (20× for the waters with 160–420 mg L⁻¹ TDS and 3× for the water with 2900 mg L⁻¹ TDS) by evaporation in a vacuum dryer at a temperature not exceeding 70°C. The lack of volatility losses during evaporation was confirmed by the coincidence of the experimental TXRF and ICP-OES results for As (see Table 2).

3. Results and discussion

3.1 Selection of mineral water samples

Three of the sources of the mineral waters analysed in the present work are located in Western Bulgaria, two – in Southern Bulgaria. Some parameters of the bottled mineral waters, as given on the bottle labels, are presented in Table 1. According to the certificates (Table 1), the ‘Gorna Bania’, ‘Kom’ and ‘Devin’ mineral waters are alkaline; ‘Thorn Spring’ is neutral while ‘Mihalkovo’ is slightly acidic (owing to its natural content of CO₂). The TDS content varies from 160–420 mg L⁻¹ (‘Gorna Bania’, ‘Kom’, ‘Devin’, ‘Thorn Spring’) to 2900 mg L⁻¹ (‘Mihalkovo’). The about 10 times higher TDS content of the ‘Mihalkovo’ mineral water may be explained with the natural presence of CO₂, which favours the leaching of the reservoir rocks. Data for the content of Na, K, Ca, Mg and Cl are given for all bottled mineral waters under examination, whereas only scarce data about the content of other trace elements are given (Table 1).

3.2 Optimisation of the conditions of the TXRF analysis

3.2.1 Effect of sample deposition

The effect of sample volume, number of pipettings/dryings and matrix (TDS) content on the area of the dry residue on the glass holder was studied. It was found that the sample volume of a single pipetting should not exceed 5 µL so that the dry residue area falls within the effective detector area (10 mm²) [24]. Sample volumes lower than 5 µL were not used owing to insufficient precision of pipetting. With a view to obtain a uniform layer of the dry residue (< 0.1 mm thick [24]) the number of consecutive pipettings/dryings should not exceed 3 for the water of higher mineralisation. Three replicates of each sample were measured at two perpendicular positions of the sample holder in order to obtain an averaged picture of the dry residue layer below the detector with a view to eliminate the effect of eventual unevenness of the layer on the precision, as recommended in ref. [17]. A similar homogeneity check is reported in ref. [21]. The six signals registered for each sample were statistically treated.

It was found that the waters of lower TDS content (‘Gorna Bania’, ‘Kom’, ‘Devin’ and ‘Thorn Spring’) gave dry residues of broader area than the ‘Mihalkovo’ water. This may be related to the lower surface tension of the low-TDS waters. In order to localise the dry residue of the low-mineralised waters within the optimum area [24] preliminary hydrophobisation of the surface of the sample holders with a silicone solution was performed (as described in the

Table 1. Parameters of the bottled mineral waters according to the certificates of the Ministry of Health of Bulgaria given on the bottle labels.

Parameter	‘Gorna Bania’	‘Kom’	‘Devin’	‘Thorn Spring’	‘Mihalkovo’
pH	9.5	9.2	9.4	7.2	6.4
TDS content, mg L ⁻¹	162	260	255	424	2914
Na, mg L ⁻¹	46.6	48	58.9	16	657
K, mg L ⁻¹	0.28	1.18		1.21	29.7
Ca, mg L ⁻¹	1.4	1.8	1.59	72.95	236
Mg, mg L ⁻¹	<0.1	<0.1	<0.1	18	49.4
Fe, µg L ⁻¹		30	10		
Mn, µg L ⁻¹		2	10		
Cd, µg L ⁻¹	<2				
Sb, µg L ⁻¹	<5				
Cl, mg L ⁻¹	2.48	1.3	3.5	2.45	48.7

Experimental). This treatment was not necessary for the analysis of the high-mineralised water ('Mihalkovo').

3.2.2 Effect of the measurement time (exposition)

The exposition was varied between 300 and 1500 s. As optimum exposition 1000 s was chosen combining low LLDs with a reasonable duration of the analysis.

Typical X-ray spectra of a low-TDS water ('Kom', 260 mg L⁻¹ TDS content) and a high-TDS water ('Mihalkovo', 2914 mg L⁻¹ TDS content) are shown in Figure 1.

3.3 Trace element content in the selected mineral waters

The following trace elements S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Br, Rb (K α lines) and Ba (La line) were determined in the water samples under the adopted experimental conditions.

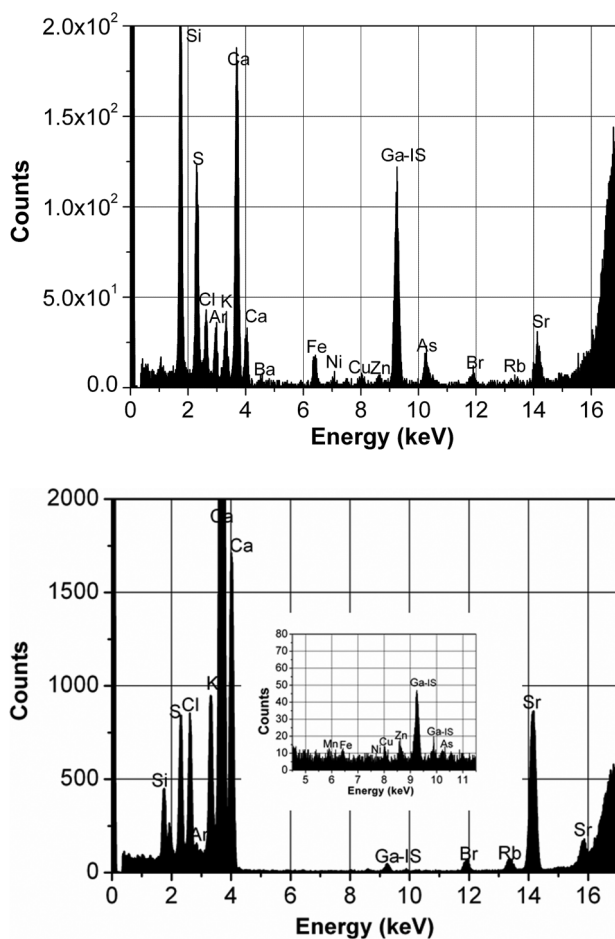


Figure 1. (a) Typical X-ray spectrum of the 'Kom' mineral water, Ga internal standard, exposition $T = 1000$ s. (b) Typical X-ray spectrum of the 'Mihalkovo' mineral water, Ga internal standard, exposition $T = 1000$ s.

Light elements (Li, Be, B and Na) were not detectable in the water samples [24]. Ag, Cd and Sb were not detected due to the low X-ray energies provided by the X-ray tube using a Mo ($Z = 42$) target. However, La X-ray lines of Ag, Cd and Sb are expected to be observed in the spectra, but such lines are unfortunately almost coincident with the $K\alpha$ X-ray lines of K and Ca causing an overlapping. The use of a Mo tube also prevents the analysis of Mo. Sr could not be determined owing to the high values (about 100) of the χ^2 -criterion calculated by the software. No lines of Al, Pb and Se were detected in the spectra of the analysed waters. No Mn was detected in the low-TDS waters ('Gorna Bania', 'Devin' 'Kom' and 'Thorn Spring'), whereas no Ba was found in the high-TDS 'Mihalkovo' water. Mg was detected in the 'Thorn Spring' and 'Mihalkovo' waters only. It displayed, however, extremely poor precision (about 50%) and was therefore excluded from the list of analytes.

The validation of the TXRF results of the trace element analysis of the NIST 1640 and NIST 1643d freshwater reference materials (RMs) obtained with the S2 PICOFOX TXRF spectrometer was reported in [24] and recoveries between 80 and 115% were registered. Owing to the lack of RMs of appropriate pH (7.0–9.5) and TDS content (160–2900 mg L⁻¹), the TXRF data obtained in the present work were validated using an independent method (classical ICP-OES after preconcentration of the water samples by evaporation). There is a good agreement within the confidence intervals of the experimental TXRF and ICP-OES data shown in Table 2. The data for the trace element content in the 'Gorna Bania', 'Devin' and 'Mihalkovo' mineral waters sampled at the corresponding source in the period 1987–1995 [1] are of the same order of magnitude, which is an indication for the rather constant trace element content of the examined mineral waters over the years.

The precision of the TXRF results for the trace element content is characterised by an RSD of 5–16%. No relationship was found between the precision of the results and the mineralisation of the water.

The TXRF lower limits of detection (LLD, $\mu\text{g L}^{-1}$) determined according to the 3σ criterion [24] in the analysed low- and high-TDS waters are shown in Figure 2. They are determined at the element concentrations given in Table 2. The LLD values in the 'Mihalkovo' water (TDS content 2900 mg L⁻¹) are higher by a factor of 5–15 than those in the waters of lower TDS content (160–420 mg L⁻¹), which may be related to the increase in the X-ray excitation scattering and the corresponding higher background. This trend is more pronounced for the light elements [24]. The limits of detection could be lowered using longer measurement times.

4. Conclusions

The trace elements S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Br, Rb and Ba in Bulgarian bottled mineral waters of low (160–420 mg L⁻¹) and high (2900 mg L⁻¹) TDS content were determined by TXRF using gallium as internal standard. The precision of the obtained results (RSD 5–16%) did not depend on the mineralisation of the analysed water. The LLD values registered in the high-TDS water were higher by a factor of 5–15 than those in the low-TDS waters. The comparative data for the trace element content in the mineral waters, obtained by conventional ICP-OES after 20× preconcentration of the low-TDS waters and 3× preconcentration of the high-TDS water, were in good agreement with the TXRF results. It may be, hence, concluded that TXRF is a suitable method for routine trace element analysis (including S, Cl and Br) of mineral waters of TDS content in a broad range – from 160 to 2900 mg L⁻¹.

Table 2. Data for the trace element content in the bottled mineral waters. The results are presented as mean \pm SD of six replicates.

Analyte	'Gorna Bania'			'Kom'			'Devin'			'Thorn Spring'			'Mihalkovo'		
	TXRF	ICP-OES	[1]	TXRF	ICP-OES	[1]	TXRF	ICP-OES	[1]	TXRF	ICP-OES	[1]	TXRF	ICP-OES	[1]
S, mg L ⁻¹	7.9 \pm 0.4	7.5 \pm 0.3		8.9 \pm 0.2	10.2 \pm 0.7		5.1 \pm 0.8	5.3 \pm 0.4		2.8 \pm 0.4	2.2 \pm 0.2		123 \pm 13	107 \pm 6	
Cl, mg L ⁻¹	2.4 \pm 0.2	2.5 \pm 0.2 [#]	2.2 [#]	1.2 \pm 0.1	4.2 \pm 0.3 [#]		3.4 \pm 0.2	2.5 \pm 0.2 [#]	2.7 [#]	2.9 \pm 0.4	2.5 \pm 0.2 [#]		47 \pm 7	56 \pm 4 [#]	44.7 [#]
K, mg L ⁻¹	0.35 \pm 0.02	0.31 \pm 0.02	0.2	1.3 \pm 0.2	1.0 \pm 0.1		0.6 \pm 0.1	0.5 \pm 0.1	0.49	1.2 \pm 0.2	0.9 \pm 0.1		48 \pm 7	44 \pm 3	25.5
Ca, mg L ⁻¹	1.3 \pm 0.2	1.26 \pm 0.13	1.8	1.4 \pm 0.2	1.5 \pm 0.1		1.7 \pm 0.1	1.5 \pm 0.1	1.07	78 \pm 8	66.7 \pm 3.9		215 \pm 25	240 \pm 10	217
Mn, μ g L ⁻¹	*	<1	0.10	*	<1		*	<1	0.11	*	<1		48 \pm 7	18 \pm 3	18
Fe, μ g L ⁻¹	25 \pm 4	25 \pm 5	30	10 \pm 1	10 \pm 1		15 \pm 2	10.8 \pm 0.2	<5	6.0 \pm 0.8	5.0 \pm 0.6		15 \pm 2	13 \pm 2	95
Ni, μ g L ⁻¹	3.0 \pm 0.5	2 \pm 0.5	<0.2	12 \pm 1	15 \pm 1		5.0 \pm 0.5	4.0 \pm 0.5	0.30	5.0 \pm 0.8	5.0 \pm 0.6		14 \pm 2	<10	6.9
Cu, μ g L ⁻¹	6.0 \pm 0.5	4.2 \pm 0.5	0.7	6.0 \pm 0.5	4.1 \pm 0.5		3.0 \pm 0.5	2.0 \pm 0.5	0.70	<2	1.7 \pm 0.2		<10	1.6 \pm 0.2	170
Zn, μ g L ⁻¹	6.0 \pm 0.5	6.0 \pm 0.5	0.4	47 \pm 4	38 \pm 4		<2	1.2 \pm 0.2	0.9	10 \pm 1	7.0 \pm 0.6		<9	1.9 \pm 0.2	5.3
As, μ g L ⁻¹	3.0 \pm 0.5	3.0 \pm 0.2	3.1	12 \pm 2	10 \pm 0.5		<1	1.0 \pm 0.2	1.5	2.5 \pm 0.2	2.3 \pm 0.2		<7	2.6 \pm 0.2	45
Br, mg L ⁻¹	8 \pm 1			37 \pm 5			6.0 \pm 0.5			15 \pm 2			0.40 \pm 0.05		
Rb, μ g L ⁻¹	5.0 \pm 0.5		28.6	4.0 \pm 0.5			<1		2.5	<1			163 \pm 25		150
Ba, μ g L ⁻¹	45 \pm 7		20	30 \pm 5			38 \pm 5		40	28 \pm 4	23 \pm 3		*	14 \pm 2	35

*not detected in the TXRF spectrum.

[#]photometric determination.

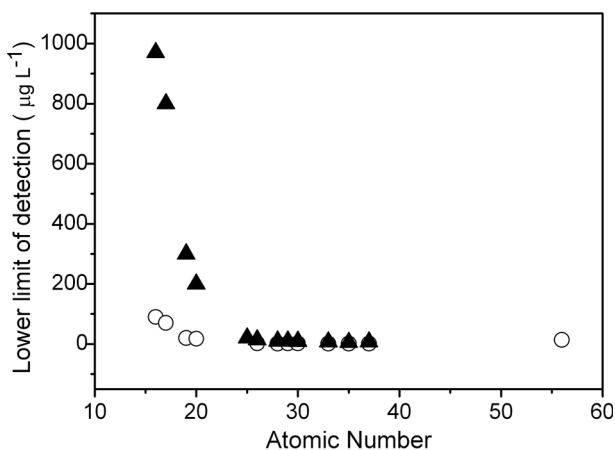


Figure 2. TXRF lower limits of detection (LLD, $\mu\text{g L}^{-1}$) in the analysed waters of low (\circ) and high (\blacktriangle) TDS content.

Acknowledgement

The authors thank the National Science Fund at the Ministry of Education, Youth and Science of Bulgaria for the financial support (Contracts DCVP-02/2/2009 and DTK 02-5/2010).

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