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CRITICAL REVIEW

Bulgarian analytical atomic spectroscopists in the new millennium—integrated in the European research area†**Dimitar L. Tsalev^{*a} and Elisaveta Ivanova^b***Received 30th May 2012, Accepted 9th August 2012*

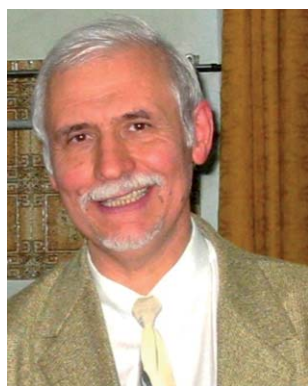
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The studies from Bulgarian analytical atomic spectroscopists in the fields of atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) and hyphenated atomic spectrometric methods after 2000 are reviewed with an emphasis on direct methods of analysis (slurry and solid sampling), rational sample pretreatment and trace elements enrichment, alternative pretreatments such as alkaline solubilization by tetraalkylammonium hydroxides, *in situ* treatment in a graphite atomizer by means of chemical modification, speciation and fractionation analysis. There is a clear focus on the development of sample preconcentration methods coupled with atomic spectrometric techniques, particularly in flow and flow injection systems to alleviate interferences and to improve limits of detection (LODs). The most notable publications concerned with methodological developments in the atomic spectroscopic analysis of environmental samples, biological and advanced materials, food and beverages, as well as speciation and fractionation studies are tabulated. Recent reviews, book chapters, bibliographies and monographs with Bulgarian authorship/co-authorship are presented. The integration of Bulgarian atomic spectroscopists in the European research area is illustrated. Some trends in the publication activities are presented.

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The aim of this review is to present research and publication activities of Bulgarian scientists in the field of analytical atomic spectrometry (AS) in the new millennium. X-ray fluorescence (XRF) techniques are not included in this review since the XRF field is outside of research and publication activities of the present authors. Articles on purely physical aspects of atomic spectroscopy and publications in Bulgarian language fall outside of its scope as a rule, hence *ca.* 15–20% of the initially collected publications have been excluded from the present discussion. We acknowledge that the review is not comprehensive as a further *ca.* 40% of relevant publications were considered in the review but not included in the final reference list. Our aim was to be critical and to provide readers with an overview of high quality Bulgarian spectroscopy research. Several pre-2000 references are given as relevant sources of information in the recent *bibliographies*,^{1,2} *reviews*,^{3–6} *book chapters*,^{7–9} and *monographs*^{10,11} on ETAAS,^{8,9} hydride generation (HG) AAS,^{6,10} chemical modification,^{2,7} hyphenated vapor generation (VG) AAS techniques,⁶ and applications of AAS in occupational and environmental health practice.^{5,11}

Early contributions of Bulgarian analysts to the field of AAS in the years 1964–1994 (456 references) were compiled and indexed by author, analyte, AAS technique, application area and other keywords by Tsalev.¹ A positive trend of the research activities and an increased percentage of publications in international editions were clearly shown in that article as mean values for earlier 5-year increments, *viz.*: nil(!), 35, 22, 33, 44 and 55% for the periods of 1965–1970, 1971–1975, 1976–1980, 1981–1985, 1986–1990 and 1991–1994, respectively. During the last 12 years about 75% of the scientific works of Bulgarian analytical atomic spectroscopists have been published in renowned international scientific journals, books and proceedings of international conferences; *ca.* 25% are published in English language in national specialized scientific journals. About one-half of scientific contributions are only of Bulgarian co-authorship.

The main Bulgarian scientific groups working in the field of analytical atomic spectroscopy, covering *ca.* 94% of examined papers, are situated at three institutions: the Faculty of Chemistry and Pharmacy (formerly Faculty of Chemistry), University of Sofia “St. Kliment Ohridski” (S. Arpadjan, R. Djingova, I. Karadjova, P. Kovacheva, I. Kuleff, V. Lyubomirova, D. L. Tsalev, B. Zlateva); the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences (N. Daskalova, A. Detcheva, G. Gentsheva, I. Havezov, E. Ivanova, S. Velichkov); and the Faculty of Chemistry, University of Plovdiv “Paisii Hilendarski” (G. Andreev, V. Kmetov, K. Simitchiev, V. Stefanova). Other contributions come from the Institute of Mineralogy and Crystallography, BAS (N. Lihareva); Geological Institute, BAS (M. Karadjov, E. N. Pentcheva, N. Velichkova); Agricultural University, Plovdiv (K. Ivanov); Regional Laboratory – Burgas, Environmental Executive Agency, Ministry of Environment and Waters (L. Chepanova), National Center for Public Health Protection, Sofia (R. B. Georgieva), *etc.*

Fruitful international cooperation with scientists and laboratories from 16 countries has been established as depicted in Fig. 1. From about 109 publications with co-authors from Europe, Turkey and Japan, productive co-works with international authors from laboratories in Belgium (21), Czech Republic (4), France (7), Germany (13), Italy (9), Spain (9), Switzerland



Fig. 1 Recent research cooperation of Bulgarian analytical spectroscopists.

(4), *etc.* and about 30 papers with scientists from neighboring Balkan countries in Bursa (3), Ljubljana (2), Skopje (24) and Thessaloniki (1) are known.

The research activities are directed towards optimization studies on the instrumental and chemical parameters of the AS methods, improvement of their metrological and technical characteristics and application studies for trace analysis of various types of samples. Approximate distribution pattern of 211 examined publications between several application fields indicates preference for environmental (~43%), agricultural, food and beverage (~22%), industrial and advanced materials (~16%), geological (~3.5%) and miscellaneous including applications to aqueous and model solutions (~5.5%). If compared with previous bibliography on AAS only,¹ this distribution demonstrates about a 2–2.5-fold decline of clinical/biological, geological and industrial application yet *ca.* 2.5-fold increase of environmental applications. Interestingly, the speciation and fractionation works (~45 papers, partly presented in Tables 2 and 3) are increased five-fold *vs.* previous periods¹ to *ca.* 23% of all application papers for the reviewed period. The approximate percentage distribution of the main analytical techniques: AAS (~61%), AFS (~4%), ICP-OES (~21%), ICP-MS (~15%) and VG with in-atomizer trapping of chemically generated species (VG-ETAAS) (~3%) is in agreement with current trends of increased role and accessibility of multielement, powerful ICP techniques. Articles on procedures and applications reveal proportions between various AAS techniques by themselves: flame atomic absorption spectrometry (FAAS) (~28%), electrothermal AAS (ETAAS) (~54%), chemical vapor generation (CVG) AAS (VGAAS) (~13%) and VG-ETAAS (4%). Thus comparison of this splitting of AAS between techniques with available data for the previous three decades 1964–1994 (60, 31, 9 and 0% for FAAS, ETAAS, VGAAS and VG-ETAAS, respectively)¹ demonstrates a reasonable contemporary decline of FAAS research in favor of ETAAS and VGAAS. The role of VG techniques with hydride generation (HG) and the cold vapor technique (CV, CVT) for mercury is also increasing, resulting in new methods such as CVAAS, HGAAS, CVAFS, HGAFS, CV-ICP-OES, HG-ICP-OES, VG-ICP-MS, as well as further hyphenations like electrothermal vaporization (ETV) in ETV-ICP-OES for multielement determinations^{12,13} and VG

Table 1 Atomic spectrometric procedures and applications briefly outlined

Analyte	Matrix	Brief procedure outline	Ref.
As	Algae; plants (citrus leaves, grass)	HNO ₃ –H ₂ O ₂ –HF dign; USN-ICP-OES; validation with CRMs	98
As	Aq. solns, org. solvents	CF-HGAAS; org. solvent interf. (MeOH, EtOH, i-PrOH, ethanolamine, acetonitrile, ethylene glycol, glycerol) studied. Atomization interf. by MeOH, EtOH and PrOH compared; three atomizers compared: QTA, Ar–H ₂ MDF and FIF; interf. minimized in FIF mode	99
As	Essential oils (lavender, rose)	4–5 fold diln with EtOH or i-PrOH; ZETAAS; THGA; L-cysteine–Pd–citric acid chem. modifier on Zr–Ir treated platforms; LODs 4.4–4.7 ng g ^{–1} ; also LTPA in oxygen; LODs 2.5–2.7 ng g ^{–1}	100
As	Fish	TMAH solubilization; ZETAAS with Pd modifier; <i>T</i> _{pyr} 1400 °C, <i>T</i> _{at} 2000 °C; LOD 0.45 µg g ^{–1}	50
As	Marine tissue CRMs	MW-assisted LLE of lyophilized tissue with TMAH or ethanol; ZETAAS; Zr–Ir permanent modifiers; FI-HGAAS; LODs 0.003–0.02 mg kg ^{–1}	51
As	Plant, sediment, soil CRMs	SS-ETAAS; US agitation of slurry; LOD 30 µg kg ^{–1} ; validation with CRMs	60
As	Urine	10 mL urine + 5 mL 0.5 M Cys + 2.5 mL 1 M HCl dild to 50 mL; batch HGAAS; LOD 0.5 ng; 15 h ^{–1}	101
As	Wine	1 mL sample + 1 mL 1% m/v Cys–0.1 M HCl; 1–10× diln; CF-HG-FAFS with Ar–H ₂ MDF; LODs 0.3–0.6 µg L ^{–1} ; alternatively bomb decomposition with HNO ₃ –H ₂ O ₂ and CF-HG-FAFS or ETAAS	20
As	Wine	Evaporation of ethanol for inorg. As; MW-assisted HNO ₃ –H ₂ O ₂ dign for total As; HGAAS	65
Au	Gold alloys	Aq. regia dign; FAAS with ASDI and ensemble summation; calibrn by a bracketing method; tutorial treatment of traceability, validation and uncertainty budget calculation	102
B	Tourmaline	Na ₂ CO ₃ –ZnO (3.5 : 0.6) dign; boron leached with H ₂ O; ICP-OES; LOD 4 µg g ^{–1}	103
Cd	Natural waters	Preconcn by flotation on Pb(II) heptyl DTC and Co(III) heptyl DTC; ZETAAS; LOD 3.0 ng L ^{–1}	72
Cd	Seawater, urine	VG-ETAAS; Cd ⁰ trapped on Zr–Ir or W–Ir treated platforms; THGA [®] ; <i>T</i> _{coll} 350 °C; <i>T</i> _{at} 1300 °C; <i>m</i> ₀ 2.8 pg; LOD 2 ng L ^{–1} ; memory effects observed	14
Co	Aq. solns	SPE in a KR pre-coated with oxine derivatives; FI-ETAAS; 34× enrichment	96
Co	Natural waters	FI; KR pre-coated with PMBP; ETAAS; LOD 8.1 ng L ^{–1}	73
Co	Natural waters, cod muscle, mussel tissue	FI; KR pre-coated with nitroso-R-salt/TBABr; ETAAS; LOD 5 ng L ^{–1} ; validation with CRMs	74
Cr	Serum, urine	Direct ZETAAS; H ₂ O ₂ modifier; validation with CRMs; LOD 0.08 µg L ^{–1}	104
Cu	Seawater	SPE on a new IIP Cu(II)–PAR; FAAS; LOD 0.001 µmol L ^{–1}	75
Fe	Seawater	SPE on anatase TiO ₂ nanoparticles; ICP-MS; validation with CRM; LOD 69 ng kg ^{–1}	76
Hg	Fish, liver, kidney, plant, soil CRMs	Direct SoS-ZETAAS; specially designed furnace; lack of matrix effects; calibrn with CRMs; LOQ 0.008 µg g ^{–1}	61
Hg	Wine	MW-assisted or under reflux dign with HCl–H ₂ O ₂ ; LLE of APDC, chloride or iodide complexes with IBMK; ETAAS using different Pd modifiers; CVAAS; LOD 0.2 µg L ^{–1}	67
Hg	Seawater, mineral water	SPE on a new IIP; CF-CVAAS; LOD 0.006 µg L ^{–1} . Synthesis and characterization of IIP microbeads by cross-linking dispersion copolymerization of methacrylic acid and trimethylolpropane trimethacrylate in acetonitrile detailed	77
Na	Single crystals of KTiOPO ₄ or KGd(WO ₄) ₂	Slurry in 2% HNO ₃ –0.005% Triton-X-100; SS-ETAAS; Ti-coated or W-coated GT, resp.; RSD 3%; good agreement with FAAS after digestion	63
Ni	Serum, urine	ZETAAS; H ₂ O ₂ modifier; LOD 0.2 µg L ^{–1} ; validation with CRMs	105
Pb	Ag, Cu, and their alloys	Electrochemical Pb sepn; ICP-OES; AAS; lead isotope ratios detn by ICP-MS; archaeometry; validation with CRMs	95
Pb	Plant, sea water	HNO ₃ –H ₂ O ₂ dign; ID-ICP-MS; ID-HG-ICP-MS; pH effect critical; ID mode preferred for better accuracy and precision	45
Pb	Wine	ETAAS; Pd modifier; 1 : 1 sample diln with 0.2 M HNO ₃ ; LOD 0.9–1.8 µg L ^{–1}	68
Pb	Wine	10× diln; CF-HGAAS with miniature Ar/H ₂ diffusion flame in the presence of 1% m/v K ₃ [Fe(CN) ₆]–0.1 M HCl; LOD 0.3 µg L ^{–1} ; alternatively direct ETAAS	69

Table 1 (Contd.)

Analyte	Matrix	Brief procedure outline	Ref.
Pd	Blood, road dust	FI enrichment by sorption of $\text{Pd}(\text{SCN})_4^{-2}$ onto KR pre-coated with $\text{K}^+18\text{-crown-6}$; ETAAS; LOD 16 ng L^{-1}	97
Pd	Tunnel dust	FI-ETAAS, sepn and preconcn using a cyclic polyether (18-crown-6) previously immobilized on a KR; LOD 16 ng L^{-1}	88
REEs	Eu_2O_3 , Lu_2O_3	ICP-OES; spectral interferences in REE matrices assessed; Q -values tabulated	17
REEs	Soils, sediments	Cation-exchange sepn; ICP-OES; validation with CRMs; LODs $0.05\text{--}0.5 \text{ mg kg}^{-1}$	93
Se	Blood serum, hair, urine	1 + 2 dilt of serum; $10 \mu\text{g Rh}$ modifier; 1 + 2 to 1 + 4 dilt of urine, $20 \mu\text{g Rh}$ modifier; hair solubilized with TEAH; ZETAAS ($\text{THGA}^{\text{®}}$); LOD $6 \mu\text{g L}^{-1}$; alternatively FI-HG-ETAAS or CF-HG-NDAFS procedures for urine digests	54
Tl	Natural waters	SPE; Empore [™] chelating disc; ZETAAS; uncoated GT; modifier-free; effect of humic acids	78
Tl	Wine	$\text{HNO}_3\text{--H}_2\text{O}_2$ dign; LLE from 0.5 M KI soln with IBMK; ZETAAS; tartaric acid or Pd + ascorbic acid chemical modifiers; LOD $0.05 \mu\text{g L}^{-1}$	66
As, Hg	Sunflower oil	Sample solubilization with TMAH for As; LLE of As and Hg with $\text{NH}_4\text{OH/EDTA}$; ZETAAS; LODs 2 ng g^{-1} As, 3 ng g^{-1} Hg	49
As, Se	Plants, soils, sediments	SS-ETAAS; mixed Ir–Mg modifier; var. mineralization modes evaluated; validation with CRMs	62
Cd, Pb	Blood, tissues (hair, liver, muscle), urine, water	Direct injection for liq. samples; TEAH solubilization for biol. tissues; phosphate modifier stabilized on pre-treated platforms with Zr–Ir or W–Ir; m_0 $0.7\text{--}1.0 \text{ pg Cd}$, $26\text{--}31 \text{ pg Pb}$	38
Cd, Pb	Bovine liver and orchard leaves SRMs	APDC complexes sorbed on C18 column; TS-flame-furnace AAS; LODs 7 ng L^{-1} Cd; 170 ng L^{-1} Pb; validation with CRMs	44
Na, Fe	Single crystals of RbTiOPO_4	Slurry in $2\% \text{ HNO}_3\text{--}0.005\% \text{ Triton-X-100}$; SS-ETAAS; TiC-coated GT	64
Pd, Pt	Airborne particulate matter, serum, urine	MW-assisted SPE; thiourea-modified silica gel; ICP-MS; LOD 0.2 ng L^{-1} ; validation by CRMs	26
Pd, Pt	Street dust, road dust	IE on Dowex 1×10 ; elution with thiourea at 60°C ; ICP-OES; R 98%; LOD 15 ng g^{-1} ; agreement with ICP-MS results	27
As, Sb, Tl	Aq. solns	ETAAS; GT with refractory metal platforms; W coil on a Ta platform recommended; $2 \mu\text{g Pd}$ modifier	41
Au, Pd, Pt	Cu ore and concentrate; soils, river water, seawater	SPE with Cys-modified SiG; ZETAAS; ICP-OES; LODs $0.02\text{--}0.005 \mu\text{g L}^{-1}$	28
Ca, Fe, Mn	Moss	ASDI-FAAS flame microsampling for plant digests; comparison with ICP-MS	106
Cd, Pb, Zn	Oak leaves	Dign with $\text{HNO}_3\text{--H}_2\text{O}_2$; USN-ICP-OES. Oak leaves as bioindicators; evaluation of air pollution; drawing of heavy metal fallout maps	90
Ga, Ho, Tm	Optical crystals of potassium titanyl phosphate	Dign with $\text{HF--H}_2\text{SO}_4\text{--H}_2\text{O}_2$; ICP-OES; study of spectral interferences in a K-, P- and Ti-containing matrix	31
Pd, Pt, Rh	Auto catalyst (recycled), CRM SARM 7, Pt ore	ICP-OES with radial viewing 40.68 MHz plasma; study of spectral interferences in environmental matrices; LODs in ng g^{-1} : 1700 Pt , 1440 Pd and 900 Rh ; LODs at var. λ tabulated; validation with CRMs	29
Pd, Pt, Rh	Pharmaceutical products (Tritace, Vivace, Laprilen, Enalapril)	Acceleration of CPE by MW ($9\times$ faster) and US irradiation; Triton-X-100; 2-mercaptobenzothiazole; acceleration of complex formation by reducing agents (KI and SnCl_2) examined; surfactant-rich concentrate phase dild with 1 M HCl prior to CF-ICP-MS; LODs $1\text{--}6 \text{ ng L}^{-1}$	46
Pd, Pt, Rh	Road dust	ICP-MS; spectral interferences investigation; uncertainty budget analysis and interference alleviation by preliminary acid leaching	107
Pd, Pt, Rh	Road dust, serum, urine	On-line FI enrichment in a KR with diethylthiourea; ICP-TOFMS with USN; LODs $0.36\text{--}2.1 \text{ ng L}^{-1}$	25
REEs, Sc, Y	Dy_2O_3 , Ho_2O_3 , Tb_2O_3 , Tm_2O_3	ICP-OES; spectral interf. in REE matrices assessed; best λ and LODs tabulated	34
REEs, Sc, Y	Gd_2O_3 , Er_2O_3	ICP-OES; spectral interf. in REE matrices assessed; best λ and LODs tabulated	30
REEs, Sc, Y	Yb_2O_3	ICP-OES; spectral interf. in REE matrix assessed; best λ and LODs tabulated	32
Cd, Co, Cu, Ni	Aq. solns	FAAS; uncertainty budget contributions from the flame, light source and optics; combined instrumental uncertainty evaluated	108
Cd, Cr, Ni, Pb	Plant CRMs	Dry mineralization followed by acid leaching; fast furnace programme ETAAS; Ir permanent modifier; validation with CRMs	37

Table 1 (Contd.)

Analyte	Matrix	Brief procedure outline	Ref.
Cd, Cu, Ni, Pb	Seawater	SPE on monodisperse, submicrometer silica spheres modified with 3-aminopropyl-trimethoxysilane; <i>in situ</i> sampling and preconcn; ETAAS; LODs 0.002–0.02 $\mu\text{g L}^{-1}$	79
Cd, Cu, Pb, Zn	Effervescent vitamins with micro-minerals	MW-assisted CPE with APDC and Triton X-100 at pH 7.5; collected surfactant-rich phase dissolved with 3 M HNO_3 ; prior to ASDI-FAAS microsampling (350 μL)	42
Cd, Pb, Cu, Zn	Plant oil crops (peanuts, rapeseed, sesame); plant parts (roots, stems, leaves, seeds, fruit shell); soil	<i>Aq. regia</i> dign of soils. Soil extracts in 5 mM DTPA–0.1 M TEA, pH 7.3. Plant tissues dry ashed at 400 °C; 1 + 1 HNO_3 treatment; final solns in 20% v/v HCl; ICP-OES; std solns in 2% v/v HNO_3 . The effect of pollution at different distances from a non-ferrous metal plant detailed	109
Cd, Hg, Mn, Pb	Algae	Direct SoS-ZETAAS; LODs 0.0013–0.008 $\mu\text{g g}^{-1}$; validation with CRMs	110
Ca, K, Mg, Mn, Na	Fluid inclusions in quartz	Opening of fluid inclusions by crushing or decrepitation of the quartz samples; leaching of the released components by HNO_3 or CDTA; FAAS; ETAAS	111
Cd, Cu, Hg, Ni, Pb	Surface waters	Preconcn on Cys-modified chitosan membrane; elution with thiourea–HCl; ZETAAS; LOQs 0.001–0.05 $\mu\text{g L}^{-1}$; LOD 0.012 $\mu\text{g L}^{-1}$ for Hg by CF-CVAAS	80
Cd, Hg, Mn, Pb, Sn	Seafood CRMs (cod muscle, mussel tissue, tuna fish, plankton, salmon, trout)	Direct SoS-ZETAAS (modifier-free); A_p measurements for Hg, A_{int} and 3-field mode for other analytes; LODs (pg): Cd 1.3, Hg 40, Mn 12, Pb 8 and Sn 70; calibrn with CRMs of organic matrices	112
Fe, Li, Nb, Sr, Ti	Single crystals of the $\text{SrO-Li}_2\text{O-Fe}_2\text{O}_3\text{-TiO}_2$ system	HF– H_3BO_3 dign; stabilization by 6.5% HNO_3 –0.05% HBF_4 ; ICP-OES; 0.04–0.08% H_3BO_3 well tolerated; matrix-matched calibrn; detn of single crystals composition	58
Ir, Pd, Pt, Rh, Ru	Moss, Pt ore, road dust, sediment	MW-assisted dign with HCl– HNO_3 ; ICP-MS; validation with CRMs; LODs 0.015–0.03 ng g^{-1}	113
As, Bi, Hg, Se, Sn, Tl	Marine sediments, water	ICP-OES; quantification of spectral interferences in environmental matrices; LODs 0.3–0.9 $\mu\text{g g}^{-1}$; validation with CRMs	56
Ba, Cd, Cr, Mn, Pb, Zn	Atmospheric particulate matter	Samples collected by the Bergerhoff method; <i>aq. regia</i> dign; ICP-OES; FAAS; d.c. arc OES	55
Cd, Co, Cu, Ni, Fe, Pb	Natural waters, sea water	SPE on a polycarboxylic microsphere gel; ETAAS; validation with CRM; LODs 0.005–0.05 $\mu\text{g L}^{-1}$	81
Cd, Cr, Cu, Fe, Mn, Pb	Lavender plant and oil	Oil dild 1 + 1 or 1 + 2 m/m with 1,4-dioxane. Wet dign of plant with HNO_3 and H_2O_2 ; FAAS; ZETAAS; permanent modification of GT with W and Pt; T_{pyr} 900, 1300, 1200, 1200, 1200 and 900 °C for Cd, Cr, Cu, Fe, Mn and Pb, resp.	114
Ag, Cd, Co, Ni, Pb, U, Y	Natural waters	FI enrichment in a KR pre-coated with PMBP; ICP TOFMS with USN; LODs 0.3–15.2 ng L^{-1}	82
Be, Bi, REEs, Te, Th, U, Y	Soils, sediments	Overnight stay with HF– HNO_3 ; subsequent stepwise MW dign with HF– H_3BO_3 ; ICP-MS; validation with CRMs	47
Cd, Co, Cr, Cu, Fe, Ni, Pb	Milk, cheese, chocolate	Wet digestion with $\text{HNO}_3\text{-HClO}_4\text{-H}_2\text{O}_2$; slurry preparation in $\text{HNO}_3\text{-H}_2\text{O}_2$; ETAAS analysis of solutions and slurries, compared with DPCSV; validation with CRMs	115
Be, Bi, Ga, REEs, Te, Tl, Th, U	Leaves (poplar)	MW-assisted dign with $\text{HNO}_3\text{-H}_2\text{O}_2$; ICP-MS; poplar leaves as bioindicator studied; distribution patterns; background conc. levels of elements tabulated	116
Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	Sewage sludge	US-assisted extraction (20 min sonication at 90 °C in $\text{HNO}_3\text{-HCl}$ (1 : 1); ICP-OES	87
Ag, Cd, Co, Cu, In, Mo, Ni, Pb, Sb	Natural waters, cod muscle, mussel tissue	FI enrichment of APDC complexes in a KR; ICP-TOFMS with USN; LODs between 0.5 and 26 ng L^{-1} ; validation with CRMs	83
Al, As, Ba, Mg, Pb, Sr, V, Zn, Zr	Archaeological bones	Dry ashing followed by MW-assisted dign with HNO_3 ; ICP-MS; validation with CRM; reconstruction of paleodiet; archaeometric study	92
As, Cd, Bi, Hg, Pb, Sb, Se, Sn, Tl	Aq. solns	ETAAS; 100 $\mu\text{g Ag}$ modifier for atomization from the wall or from a platform; 1.2–1.8 \times sens. enhancement by an Ag modifier	36
Bi, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb	Lavender oil	Diln with i-PrOH (1 + 1) or 1,4-dioxane (1 + 2); ETAAS; W-treated or W–Pt treated GTs	117
As, Cd, Co, Cu, Hg, Fe, Mn, Ni, Pb, Zn	Sediment, sludge, soil	MW-assisted dign with <i>aq. regia</i> ; FAAS; ICP-MS; ICP-MS with temp. controlled MW-assisted dign recommended; validation with CRMs	48
Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, Zn	Archaeological bones	ICP-OES; IE enrichment on Dowex 1 \times 10 resin for Cu(II); 3 nebulizers compared: concentric-flow (Meinhard), cross-flow and V-groove; spectral interf. tabulated; validation with CRM; reconstruction of paleodiet; archaeometric study	91

Table 1 (Contd.)

Analyte	Matrix	Brief procedure outline	Ref.
Ce, Ir, La, Nd, Pb, Pd, Pt, Rh, Ru, Zr	Street dust, plants (dandelion, annual ryegrass, plantain, moss, mushrooms)	MW-assisted dign with HNO ₃ and HCl for ICP-MS; LLE of Pd(II)-DEDTC with CHCl ₃ ; <i>aq. regia</i> dign for ICP-OES; validation with CRMs; accumulation of PGE by plants along highways evaluated	89
Al, Ca, Co, Cr, Cu, Fe, K, Na, Mg, Mn, Ni, Sb	Archaeological glasses	Direct ETV-ICP-OES analysis of powdered microsamples; calibration with CRMs; CHF ₃ gaseous modifier	13
Ag, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Pd, Pt, Sb	Au	Reductive pptn of Au matrix by oxalic acid; ETAAS; ICP-OES; LOQs 0.02–0.1 µg g ⁻¹ or 0.3–2.4 µg g ⁻¹ , resp.	94
As, Ba, Ca, Cd, Cr, Cu, Fe, Mn, Pb, Sr, U, V, Zn	Moss	Comparison between 3 methodologies for discrete sample introduction in ICP-MS; Every Sweep Internal Standardisation algorithm (ESIS) recommended; LOQs 0.02–66 mg kg ⁻¹	43
As, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se	Ag (high-purity)	Total or partial reductive sepn of Ag matrix with ascorbic acid; ZETAAS; LODs 0.001 µg g ⁻¹ Cd, 0.005 µg g ⁻¹ Mn, 0.01 µg g ⁻¹ Cr and Cu, 0.02 µg g ⁻¹ Fe, Co and Pb, 0.05 µg g ⁻¹ As, Bi, Ni, Sb and Se, 0.2 µg g ⁻¹ Hg	35
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb	Natural waters	FI enrichment in KR pre-coated with PMBP; ICP-TOFMS with USN; LODs 3–670 pg L ⁻¹	84
Al, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, S, Sr, Ti, V, Zn	Plant CRMs (apple leaves, sargasso, tobacco)	Sample pretreatment by carbonization; ETV-ICP-OES; gaseous modifiers of the Ar inner gas (CCl ₄ , CHCl ₃ , CCl ₂ F ₂ , C ₃ H ₈); freon CCl ₂ F ₂ recommended; LODs 5–250 ng g ⁻¹ ; calibrn with CRMs	12
As, Be, Bi, Cd, Co, Cr, Cu, Ga, Ni, Pb, Rb, REEs, Sr, Th, Te, V, Zn	Plants	MW-assisted dign with HNO ₃ –H ₂ O ₂ ; ICP-MS; validation with CRMs	118
Al, Bi, Cd, Co, Cr, Cu, Fe, Ga, In, Mn, Mo, Ni, Pb, Tl, V, Sb, Sn, Zn	Waters	Preconcn on high-surface area ZrO ₂ ; FI-ICP-OES	85
Al, Ce, Cr, Er, Fe, Ga, Ge, Ho, Mn, Na, Nb, Nd, Ni, Rb, Tb, Tm, Yb, Zr	Optical crystals of potassium titanyl phosphate	Dign with HF–H ₂ SO ₄ ; ICP-OES; assessment of dopants incorporation into the optical crystal	57
Al, Bi, Co, Cd, Cu, Cr, Fe, Hg, Ga, In, Mo, Mn, Ni, Pb, Sc, Tl, Ti, Sn, U, V, W, Y, Zn, Zr	Natural waters	On-line preconcn on Muromac A-1 resin; ICP-OES; LODs 0.001–0.009 µg L ⁻¹ ; validation with CRMs	86

with in-atomizer trapping of chemically generated species (VG-ETAAS, CV-ETAAS)¹⁴ (Table 1). Couplings with chromatographic techniques for speciation analysis such as gas chromatography (GC) with cryogenic trapping (CT) and AFS detection for Hg,^{15,16} liquid chromatography (LC) and high performance liquid chromatography (HPLC) for As,^{17–20} Pd,²¹ Pt²¹ and Se¹⁹ are compiled in Table 2 – see also recent reviews.^{6,22–24}

Along with the application of well-established methods, novel developments for the AS analytical techniques are reported (Table 1), where applications to numerous chemical elements are given with analytes arranged in an alphabetical order. Among the most intensively studied analytes are As, Cd, Co, Cr, Fe, Hg, Mn, Ni, Pb, Sb, Se, Tl, Zn, and platinum group metals Pd, Pt, Rh (PGMs) as emerging pollutants.^{25–28} Rare earth elements (REEs) are components of advanced materials and analytical challenge because of their spectral interferences.^{29–34} Application studies of 27 chemical elements representing interest for speciation and fractionation studies and procedures are known, partly presented

in Tables 2 and 3, respectively, with a focus on environmentally, toxicologically and nutritionally important elements As, Cd, Cr, Cu, Fe, Hg, Pb, Sb, Se, Sn and Zn, and PGMs.

Systematic studies are performed on the optimization of the instrumental parameters of AS detection methods. Silver is proposed as a new modifier for the ETAAS determination of volatile elements;^{35,36} four gaseous chemical modifiers in ETV-ICP-OES are studied;¹² the advantages of an Ir permanent modifier in fast ETAAS programs are demonstrated.³⁷ Several contributions on chemical modification with an emphasis on permanent modifiers in ETAAS and VG-ETAAS are published.^{3,4,7,38,39} Chemically modified platforms^{38–40} and refractory metal platforms are studied for ETAAS.⁴¹ A bibliography on earlier chemical modification literature in ETAAS for the period 1973–1989 with 560 references indexed by authors, matrix, modifier and other keywords is published.²

Sample introduction in AS methods has been the subject of thorough studies, *e.g.*, the development of air-segmented discrete

Table 2 Speciation studies and procedures briefly outlined

Element	Species	Matrix	Brief procedure outline	Ref.
As	As(III) + As(V) + MMA + DMA; total As	Marine tissues (algae, aq. plant, fish, liver, mussel, oyster CRMs)	Pressurized MW extrn with TMAH or aq. 80% v/v MeOH; ZETAAS with THGA [®] ; Pd modifier on a Zr–Ir treated platform; LOD 1.2 mg kg ^{−1} total As. Hydride active fraction by FI-HG-ETAAS in 60–90 mM HCl–75 mM Cys; LODs 3–20 µg kg ^{−1} . The behavior of arsenosugars addressed. The std addn approach is inefficient in the case of species-dependent slope of the calibrn graph ('intrinsic element speciation interference') Biouptake and biotransformation of var. As species on a green microalga <i>Chlorella salina</i> in seawater studied; the effect of phosphate discussed; wet dign of algae with HNO ₃ ; FI-HGAAS and ZETAAS as detailed in ref. 51	51
As	As(III), As(V), MMA, DMA	Algae, seawater	On-line pre-redn and complexation of As species with Cys in FI-HGAAS studied. HPLC-HGAAS sepn of complexes demonstrated on a strongly acidic cation exchange column at pH 3.3–3.5; LOD 0.5 ng or 10 µg L ^{−1}	52
As	As(V), MMA, DMA	Aq. solns	MW extrn in 0.075% m/v TMAH or 20% v/v MeOH; FI-HG-ETAAS; total As by direct ETAAS; validation with CRMs	18
As	As(III) + As(V) + MMA + DMA	Fish	Selective CF-HGAAS from var. reaction media; LOD 0.1 µg L ^{−1}	50
As	As(III), As(V), MMA, DMA	Natural waters	Extrn with 50 mM EDTA, pH 6–7; CF-HGAAS; LOD 0.2 mg kg ^{−1} ; RSD 3–7%	121
As	As(III) + As(V) + MMA + DMA	Sediment and soil extracts	10–25× diln; HG from 50 mM L ^{−1} HCl–70 mM Cys medium; FI-HG-ETAAS; Zr–Ir permanent modifier; THGA [®] ; <i>T</i> _{coll} , <i>T</i> _{pyr} , <i>T</i> _{at} , <i>T</i> _{el} 450, 500, 2100 and 2150 °C, resp.; <i>m</i> _o 39 pg; LODs 0.4–1 µg L ^{−1} ; 25 h ^{−1}	127
As	As(III) + As(V) + MMA + DMA	Urine	5× diln; batch HGAAS from 50 mM HCl–70 mM Cys medium; LOD 0.5 ng; RSD 2–6%; 15 h ^{−1}	130
As	As(III) + As(V) + MMA + DMA	Urine	Evaporation of ethanol for inorg. As; MW-assisted HNO ₃ –H ₂ O ₂ dign for total As; HGAAS (i) CF-HG-FAFS with Ar–H ₂ MDF; 5–10× diln; selective HG from var. reaction media/pH; (ii) HPLC-HG-FAFS on a strongly acidic anion exchange column	101
As	Inorg. As; total As	Wine	SPE on high-surface area TiO ₂ (anatase); ETAAS; LODs 30 ng L ^{−1} for Cr ³⁺ and 24 ng L ^{−1} for Cr(VI)	65
As	As(III); As(III) + MMA; As(III) + As(V); MMA	Wine	Preconcn and speciation analysis on high-surface area TiO ₂ ; FI-ICP-OES; validation with CRMs LLE with thiocyanate/IBMK or 1,10-phenanthroline/ClO ₄ [−] /IBMK; column SPE with TOMACl on silica gel; FAAS	20
Cr	Cr(III), Cr(VI)	Natural waters	MW-assisted extrn with TMAH, methanolic KOH or 5 M HCl; CF-CVAAS, FI-CVAAS and CF-CVG-ICP-OES compared with LODs 5–7 ng g ^{−1} for inorg.-Hg(II) and 12–16 ng g ^{−1} for MeHg, resp.; validation with CRMs	53
Cr	Cr(III), Cr(VI)	Natural waters	HG-CT-GC-AFS; validation with CRMs	15
Fe	Fe(II), Fe(III)	Wines	Derivatization by HG or ethylation; cryofocussing; GC-AFS; LODs 0.22 ng L ^{−1} for Hg ²⁺ , 0.02 ng L ^{−1} for MeHg ⁺	70
Hg	Hg(II), MeHg	Fish	New sorbent L-Cys-grafted SiG evaluated; on-site SPE enrichment; CF-CVAAS vs. ICP-MS; LOQs 1.5 and 5 ng L ^{−1} for dissolved inorg.-Hg(II) and CH ₃ Hg(I) by CF-CVG-AAS and 1 and 2.5 ng L ^{−1} by ICP-MS with RSD between 7–12% and 7–14%, resp.	124
Hg	Hg(II), MeHg	Natural water	LSME of DTC complexes into xylene at pH 5–8 for Sb(III) and pH 0–1.2 for total Sb; ZETAAS; LOD 2 ng L ^{−1} ; validation with CRM	125
Hg	Hg(II), MeHg	Sediment, water	SPE on Dowex 1 × 10; Pt(II)–DEDTC elution with IBMK; PtCl ₆ ^{2−} elution with thiourea; ICP-OES; LOD 15 ng g ^{−1}	128
Hg	Hg(II), MeHg	Surface waters (spiked)	Anion exchange; IC-ICP-MS; LODs 0.4–0.8 µg L ^{−1} As, 4 µg L ^{−1} Se	19
Sb	Sb(III), Sb(V)	Natural waters		
Pt	Pt(II) and Pt(IV) chloride species	Soil (spiked)		
As, Se	As(III), As(V), MMA, DMA, AsB; Se(IV), Se(VI)	Groundwater, soil extracts		

Table 2 (Contd.)

Element	Species	Matrix	Brief procedure outline	Ref.
As, Sn	As(III), As(V), MMA, DMA, AsB, AsC, TMAO, Me ₄ As ⁺ ; inorg.-Sn(II/IV), Me ₂ Sn, Me ₃ Sn, Et ₃ Sn, Pr ₃ Sn, Ph ₃ Sn, BuSn, Bu ₂ Sn, Bu ₃ Sn	Aq. solns; urine (for As only)	On-line UV photooxidation with K ₂ S ₂ O ₈ in a KR for 6 org.-As and 10 org.-Sn species in a FI-HGAAS system evaluated with a view to coupling with a HPLC-UV-HGAAS system. LODs 7 and 4 µg L ⁻¹ for As in FI-UV-HGAAS and HPLC-UV-HGAAS systems, resp. Var. reaction mixtures evaluated for VG from var. As and Sn species; low recoveries for butylated organotin species	17
Pd, Pt	Humic acid complexes of Pd(II), Pt(II), Pt(IV)	Soil and street dust (spiked)	Complexation of Pd(II), PtCl ₄ ²⁻ and PtCl ₆ ²⁻ with humic acids studied by SEC with UV-DAD; ICP-MS quantification	21

Table 3 Selected fractionation studies and procedures briefly outlined

Element	Species	Matrix	Brief procedure outline	Ref.
As, Cd, Pb	Anion, cation, macromolecular fractions	Medicinal herbs	Fractionation scheme; MW-assisted dign with HNO ₃ ; herbal infusions in hot water; SPE on an anion-exchange resin; pptn of protein-bound element species; ICP-MS	119
Ce, La, Zr	Fractions of extracted species	Road dust	Fractionation <i>via</i> conventional sequential extraction protocol (BCR); ICP-MS; complexation with humic substances; validation with CRMs	131
Cu, Fe, Zn	Three fractions; labile complexes of Cu, Fe, Zn	Wines	Fractionation; speciation; separation of wine polyphenols, wine proteins and polysaccharides on XAD-8; separation of cationic and anionic species of analytes on Dowex ion exchange resins; FAAS; ETAAS	71
Pd, Pt, Rh	Fractions of extracted species	Soil, street dust	A 3-step BCR sequential extrn procedure; solubilization; ICP-MS; complexation with humic substances studied	129
Cd, Cu, Ni, Pb	Free ions; labile complexes; kinetically inert org. complexes	Surface waters of Black Sea coastal area	Fractionation by HF-PLM and DGT; ETAAS following LLE of DTC complexes into IBMK; the concns of Cd, Cu, Ni and Pb detd by HF-PLM are lower compared to those by DGT, <i>viz.</i> 'free' metal ions by HF-PLM and dynamic (mobile and labile) species by the DGT. Bioavailability to green microalga <i>Chlorella salina</i> studied	126
Cu, Fe, Mn, Zn	Hot water extractable elements; anion, cation, macromolecular fractions	Medicinal plants	Herbal infusions in hot water; speciation; fractionation by IE, selective pptn and LLE; ICP-MS; FAAS; bioavailability of extracted and separated fractions discussed	120

sample introduction (ASDI) for flame AAS;⁴² the studies on three discrete sample introduction systems in ICP-MS, flow injection, air segmented discrete introduction and injection into an air carrier, eventually recommending the use of the Every Sweep Internal Standardization (ESIS) algorithm for quantitative purposes.⁴³ The use of thermospray (TS) flame furnace AAS for the determination of trace amounts of Cd and Pb has been demonstrated.⁴⁴ A comparison is made between hydride generation and nebulization for sample introduction in the determination of Pb by ICP-MS with external calibration or internal standard (IS).⁴⁵ Semi-batch and FI-VG-ETAAS with different flow systems and in-atomizer trapping were applied for determination of Cd in water and urine.¹⁴

Microwave (MW) treatments are steadily adopted for intensification and 'greening' of sample pretreatment. MW assisted cloud point extraction (CPE) was successfully applied for trace amounts of Pd, Pt and Rh in various pharmaceutical products.⁴⁶

More efficient and environmentally friendly MW digestions of soils and sediments for determination of lanthanoids⁴⁷ and other elements by FAAS and ICP-MS have been developed.^{47,48} Alkaline solubilization of small samples of biological matrices such as fish and other marine tissues, food, hair, nail, liver, *etc.* with strong organic bases tetramethylammonium hydroxide (TMAH) or tetraethylammonium hydroxide (TEAH) has proved convenient and successful in ETAAS and VGAAS procedures, being compatible with VG speciation analysis procedures, as shown in some examples for As,^{49–52} Cd and Pb,³⁸ Hg,⁵³ Se,⁵⁴ *etc.*¹¹ in Tables 1 and 2.

Systematic studies are performed on the quantification of the spectral interferences in ICP-OES, which is of particular importance for the trace analysis in complex matrices, *e.g.*, the determination of trace REEs in "pure" rare earth matrices;^{30,32–34} determination of toxic and essential trace elements in environmental and geological matrices;^{55,56} and determination of

dopants and major components in optical single crystals.^{31,57,58} Best wavelength (λ) selection is addressed. The basis of these investigations is the Q -concept using the “true detection limits criterion”, developed by Boumans *et al.*⁵⁹ The quantification of the interferences is achieved in terms of Q -values for line interference $Q_l(\lambda_a)$ and wing background interference $Q_w(\Delta\lambda_a)$. The “best” analytical lines with a view to minimizing spectral interferences were selected and the true LODs by using these lines were calculated. Up to 15 REEs (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb) have been treated in these systematic studies by Daskalova and co-workers (Table 1).

A special emphasis is put on the development of slurry sampling (SS) and solid sampling (SoS) ETAAS methods for trace analysis in complex, hardly soluble matrices. These approaches are environmentally friendly and exhibit lower reagent/procedural blanks, lower contamination risk, reduced sample consumption and other positive assets. For example, SS or SoS ETAAS methods are developed for the determination of toxic trace elements such as As, Cd, Hg, Mn, Pb, and Sn in biological tissues, algae, soils and sediments,^{60–62} as well as for the determination of trace element content in single crystals of optical materials.^{63,64}

Since Bulgaria is a major producer of wines, recent research work has been devoted to the analysis of wines by developing robust, sensitive and precise methods for the determination of total concentrations of trace elements like As, Cd, Cr, Cu, Hg, Fe, Ni, Pb, Tl and Se in wines using various AS techniques (ETAAS, HGAAS, CV-AAS, VG-FAAS, FAAS),^{20,65–68} as well as their relevant fractions and chemical species.^{20,65,69–71}

Several studies are devoted to the determination of toxic trace elements in a broad variety of environmental samples such as air,²⁶ natural waters,^{14,72–86} soils and sediments,^{48,62,87} and road dusts^{25,27,88,89} with a view to evaluating environmental pollution by industrial, agricultural and traffic activities, drawing heavy metal fallout maps,⁹⁰ *etc.*

The composition of a large variety of archaeological bones has been addressed in archaeometric studies. The obtained results are used to reconstruct paleodiet.^{91,92} Major and minor constituents of medieval glasses are determined with a view to shed light on medieval recipe norms for glass production.¹³

As a result of the studies on sample pretreatment coupled to AS techniques, numerous separation and enrichment procedures are developed and optimized. Special attention is paid to the flow injection (FI) or CF (continuous flow) on-line coupling of preconcentration procedures with the subsequent AS detection techniques such as ETAAS, ICP-OES and ICP-MS. Solid phase extraction (SPE) procedures using sorbent nano- and microbeads are proposed for the enrichment of metal ions from waters and biological fluids;^{26,28,76,79–81,85} ion exchangers and chelating resins are evaluated with the same purpose.^{27,78,86,93} Preconcentration on new ion imprinted polymers (IIPs) is used for the determination of Cu in waters.⁷⁵ Preconcentration of a large number of analytes is realized by liquid–liquid extraction (LLE) of their chelate complexes, chlorides or iodides in isobutylmethyl ketone (IBMK)^{66,67,87} or by flotation.⁷² Cloud point extraction (CPE) preconcentration procedures are applied to the determination of PGMs in pharmaceutical preparations.⁴⁶ Reductive precipitation of the matrix is applied for the determination of trace elements in high-purity gold⁹⁴ and silver.³⁵

Electrochemical separation of Pb is used prior to its isotope ratio determinations in Ag, Cu and their alloys in archaeometric investigations.⁹⁵

A series of studies is devoted to the optimization of the FI preconcentration of trace elements as chelate complexes in a knotted reactor (KR) and its on-line coupling with ETAAS using various chelating reagents and preconcentration techniques.^{73,74,88,96,97} The FI system is further modified with a view to its on-line coupling with ICP-time-of-flight(TOF)-MS.^{25,82–84}

Analytical procedures using solid phase extraction (SPE), ion exchange (IE), LLE, as well as fractionation schemes were developed for the speciation determination of toxic elements like As, Cr, Hg, Tl, Fe, Pt, Sb, and Se in various food items,^{50,51,53} beverages,^{118–120} natural waters,^{15,19,52,121–126} soils and sediments,^{16–21,127–129} body fluids and tissues,^{17,101,130} road dust,¹³¹ *etc.*, with a view to assess bioavailability, biotransformations and distribution patterns.

The metrological characterization of the AS methods, providing metrological traceability and uncertainty budget evaluation, is addressed in several papers.^{61,102,107,108}

Bulgarian analytical atomic spectroscopists have contributed *chapters* in encyclopedia¹³² and scientific *books* on AAS,¹³² AAS in environmental, biological and food analysis,²⁴ palladium in environmental materials,¹³³ analysis of Au alloys by FAAS as a practical example on traceability, measurement uncertainty and validation,¹⁰² as well as *reviews* on ICP-MS using FI on-line preconcentration and time-of-flight mass analyser (ICP-TOF-MS),¹³⁴ “VG or ETAAS—Both”,²² advances, anticipations and reality with permanent modification in ETAAS,³⁹ speciation analysis for Hg in the aquatic environment,²³ SPE in the determination of Au, Pd and Pt,¹³⁵ VG techniques for Cd,¹⁴ and analysis of wine.¹³⁶

The above survey indicates that the research activities of Bulgarian atomic spectroscopists in the new millennium have led to noticeable contributions to the field of analytical atomic spectroscopy like methodological improvements in sample pretreatment, chemical modification, trace element enrichment, quantification of spectral interferences in ICP-OES with an emphasis on REEs, development of speciation and coupled techniques, as well as in numerous application studies. Substantial progress in international visibility of research results and their documentation has been reached in the recent two decades. The role of international cooperation between Bulgarian and European scientists, realized by joint projects, research stays, and informal contacts and collaborations, is gradually increased by involving younger researchers.

An outlook on near future for Bulgarian atomic spectroscopy, although uncertain, is worth attempting. On the basis of the authors' experience and knowledge of available research facilities, current (mainly academic) staff resources, international research links and proximate projects it could be expected that some traditional research and application fields such as trace element enrichment, speciation analysis, characterization of novel/advanced materials and metal complexes, environmental analysis, improving analytical methodology for emerging (micro, nano) pollutants, food and agriculture, water (with high TDS) and plant analysis, and archaeometric investigation would be continued. There are good prospects for analytical developments and applications to food, beverages and food additives,

particularly local food items such as fish, wine, spirits, juices, honey, herbs and teas, nuts, plant extracts, vegetable oils, essential oils, as well as pharmaceutical research and development. Metrological aspects of analysis (thorough validation, uncertainty budgeting, robustness, selectivity, reference materials) will be continuative. The general trends to environmentally friendly treatments and methodologies (UV, sonication, MW, scaling down, *etc.*) in digestion, enrichment and quantification would be considered. Moderate progress in research on novel materials in sample preparation schemes (IIPs, MIPs, nanosized materials, novel reagents, *etc.*) is anticipated. Some decline of FAAS, ETAAS and CVG would be expected, while research and novel developments on multielement plasma-based techniques will grow. Publication activities are expected to stabilize at a reasonable level of 75–80% in international journals, with over 50% international co-authorship. Further success owing to the imagination and creativity of the younger generation of students and researchers is an optimistic expectation.

List of abbreviations

A_{int}	Integrated absorbance (peak area measurements)	dign	Digestion
A_{p}	Absorbance (peak height measurements)	dild	Diluted
AAS	Atomic absorption spectrometry	diln	Dilution
addn	Addition	dissoln	Dissolution
AFS	Atomic fluorescence spectrometry	DMA	Dimethylarsinate
APDC	Ammonium pyrrolidinedithiocarbamate	DPCSV	Differential pulse cathodic stripping voltammetry
aq.	Aqueous	DTC	Dithiocarbamate
<i>aq. regia</i>	<i>Aqua regia</i> ($\text{HNO}_3\text{--HCl}$, 1 : 3 v/v)	DTPA	Diethylenetriaminepentaacetic acid
AS	Analytical atomic spectrometry	EDTA	Ethylenediaminetetraacetic acid
AsB	Arsenobetaine	EPXMA	Electron probe X-ray microanalysis
AsC	Arsenocholine	eqn	Equation
ASDI	Air-segmented discrete sample introduction	ETAAS	Electrothermal atomic absorption spectrometry
BCR	Community Bureau of Reference	ETV	Electrothermal vaporization
BICIN	<i>N,N</i> -Bis(2-hydroxyethyl)-glycine	extrn	Extraction
C_0	Characteristic concentration	FAAS	Flame atomic absorption spectrometry
calibrn	Calibration	FAFS	Flame atomic fluorescence spectrometry
CDTA	Cyclohexane-1,2-diamine- <i>N,N,N',N'</i> -tetraacetic acid	FI	Flow injection
CF	Continuous flow	FIF	Flame-in-flame
corrn	Correction	FIT	Flame-in-tube
CPE	Cloud point extraction	GC	Gas chromatography
CRM	Certified reference material	GT	Graphite tube
CT	Cryogenic trap (trapping)	HF-PLM	Hollow fiber permeation liquid membrane
CV	Cold vapor	HG	Hydride generation
CVAAS	Cold vapor atomic absorption spectrometry	HGAAS	Hydride generation atomic absorption spectrometry
CVAFS	Cold vapor atomic fluorescence spectrometry	HMA-	Hexamethylene ammonium
CVG	Chemical vapor generation	HMDTC	hexamethylenedithiocarbamate
CVT	Cold vapor technique	HPLC	High performance liquid chromatography
Cys	L-Cysteine	IBMK	Isobutylmethyl ketone
DAD	Diode array detector	IC	Ion chromatography
d.c.	Direct current	ICP	Inductively coupled plasma
DEDTC	Diethyldithiocarbamate	ICP-MS	Inductively coupled plasma mass spectrometry
detd	Determined	ICP-OES	Inductively coupled plasma optical emission spectrometry
detn	Determination	ID	Isotope dilution
DGT	Diffusion gradients in thin-film gels	IIP	Ion imprinted polymer
		inorg.	Inorganic
		interf.	Interference
		IRMM	Institute for Reference Materials and Measurements (Geel, Belgium)
		IS	Internal standard
		IE	Ion exchange
		KR	Knotted reactor
		LC	Liquid chromatography
		LLE	Liquid–liquid extraction
		LOD	Limit of detection
		LOQ	Limit of quantitation
		LSME	Liquid semi-microextraction
		LTPA	Low temperature plasma ashing
		m_0	Characteristic mass for integrated absorbance measurements
		m_{p}	Characteristic mass for peak height measurements
		MDF	Miniature diffusion flame
		MMA	Monomethylarsonate
		MS	Mass spectrometry

m/v	Mass/volume
MW	Microwave
ND	Non-dispersive
OES	Optical emission spectroscopy (spectrometry)
org.	Organic (organo-)
PAR	4-(2-Pyridylazo)resorcinol
PGM	Platinum group metal
PMBP	1-Phenyl-3-methyl-4-benzoyl pyrazolone-5
ppt	Precipitate
pptn	Precipitation
preconcn	Preconcentration
QTA	Quartz tube atomizer
R	Recovery
REE	Rare earth element
RM	Reference material
RSD	Relative standard deviation
sens.	Sensitivity
sepn	Separation
SEC	Size exclusion chromatography
SiG	Silica gel
SoS	Solid sampling
SPE	Solid phase extraction
SRM [®]	Standard reference material
SS	Slurry sampling
std	Standard
STPF	Stabilized temperature platform furnace
T_{at}	Atomisation temperature
T_{cl}	Clean temperature
T_{coll}	Collection (trapping) temperature
T_{pyr}	Pyrolysis temperature
T_{vap}	Vaporization temperature
TBA	Tributylammonium
TDS	Total dissolved solids
TEA	Triethanolamine
TEAH	Tetraethylammonium hydroxide
THGA [®]	Transverse heated graphite atomizer
TMAH	Tetramethylammonium hydroxide
TMAO	Trimethylarsineoxide
TOF	Time-of-flight
TOFMS	Time-of-flight mass spectrometry
TOMACl	Tri- <i>n</i> -octylmethylammonium chloride
TS	Thermospray
US	Ultrasonic
USN	Ultrasonic nebulizer
UV	Ultraviolet (treatment)
var.	Various; variable
VG	Vapor generation
VGAAS	Vapor generation atomic absorption spectrometry
VGAFS	Vapor generation atomic fluorescence spectrometry
VG-FAFS	Vapor generation flame atomic fluorescence spectrometry
vol.	Volume
v/v	Volume/volume
XRF	X-ray fluorescence
ZETAAS	ETAAS with Zeeman-effect background correction

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