BABEȘ-BOLYAI UNIVERSITY OF CLUJ-NAPOCA

FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

CHEMISTRY DEPARTMENT

ANALYTICA RESEARCH CENTER

ABSTRACT OF PHD THESIS

MINIATURIZED INSTRUMENTATION WITH MICROPLASMA SOURCE AND ANALYTICAL APPLICATIONS FOR DETERMINATION OF TOXIC ELEMENTS FROM LIQUID SAMPLES BY OPTICAL EMISSION SPECTROMETRY

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Microplasma technology

Capacitively coupled plasma microtorch

Miniaturized SSETV-µCCP-OES prototype instrumentation

Simultaneous multi-elemental determination from liquid microsamples by SSETV-µCCP-OES

Electrothermal vaporization with Rh filament

Mercury determination by CV-µCCP-OES and SICV-µCCP-OES

Sono-induced cold vapour derivatization

Validation of SSETV-µCCP-OES, CV-µCCP-OES, SICV-µCCP-OES methods

Unsupervised chemometric modeling of groundwater with high natural As content

Chemical modeling of behavior – occurance of As species in groundwater

LIST OF ABBREVIATIONS

AFS	Atomic fluorescence spectrometry
CA	Cluster analysis
CCD	Coupled charge device
CCMP	Capacitively coupled plasma with parallel plate electrodes
CMA	Maximum concentration accepted
CRM	Certified reference material
CV-AAS	Cold vapour atomic absorption spectrometry
CV-AFS	Cold vapour atomic fluorescence spectrometry
CV-μCCP-OES	Cold vapour capacitively coupled microplasma optical emission spectrometry
CV-DBD-OES	Cold vapour dielectric barrier discharge optical emission spectrometry
CVG-μAPGD-OES	Cold vapour generation atmosferic pressure glow microdischarge optical emission spectrometry
CV-ICP-OES	Cold vapour inductively coupled plasma optical emission spectrometry
CV-ICP-MS	Cold vapour inductively coupled plasma mass spectrometry
CV-MSP-OES	Cold vapour microwave microstrip plasma optical emission spectrometry
CV-Pdc-OES	Cold vapour atmospheric pressure pulsed direct current microplasma optical emission spectrometry
DBD	Dielectric barrier discharge
EC	Electrical conductivity
EFSA	European Food Safety Authority
E_h	Redox potential
ETV-DBD-OES	Electrothermal vaporization dielectric barrier discharge optical emission spectrometry
ETV-MPD-OES	Electrothermal vaporization alternative current microplasma optical emission spectrometry
FAAS	Flame atomic absorption spectrometry

FHCC	Fuzzy hierarchical cross-clustering
FLA-APGD	Flowing liquid anode atmospheric pressure glow discarge
FLC-APGD	Flowing liquid cathode atmospheric pressure glow discarge
FPCA	Fuzzy principal component analysis
FWHM	Full width at half maximum
GAC	Green analytical chemistry
GC-DBD-OES	Gas chromatography dielectric barrier discharge optical emission spectrometry
GC-ICP-MS	Gas chromatography inductively coupled plasma mass spectrometry
GC-MHCD-MS	Gas chromatography microhollow cathode discharge mass spectrometry
GD-µ-AED	Gas chromatography atomic emission microdetector
GFAAS	Graphite furnace atomic absorption spectrometry
HG-µCCP-OES	Hydride generation capacitively coupled microplasma optical emission spectrometry
HPLC-ICP-MS	High performance liquid chromatography inductively coupled plasma mass spectrometry
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MCL	Maximum contamination level
MHCD	Microhollow cathode discharge
mICP	Microfabricated inductively coupled plasma
MPD	Microplasma device
MPT	Microwave plasma torch
MSE	Micro-structured electrode
MSP	Microwave microstrip plasma
NBL	Natural background level
NPK	NPK complex fertilizers
OES	Optical emission spectrometry
OSIM	State Office for Inventions and Trademarks

PCA	Principal component analysis
PCB	Polychlorinated biphenyl
PP-CCP	Atmospheric pressure parallel plate capacitively coupled plasma
PRSD	Predicted relative standard deviation
PTFE	Polytetrafluoroethylene
rfCCP	Radio frequency capacitively coupled plasma
RSD	Relative standard deviation
RSDB	Relative standard deviation of background
SBR	Signal-to-background ratio
SCP	Stabilized capacitive plasma
SICV	Sono-induced cold vapour generation
SICV-μCCP-OES	Small sized electrothermal vaporization capacitively coupled microplasma optical emission spectrometry
SSETV-μCCP-OES	Electrothermal vaporization capacitively coupled microplasma optical emission spectrometry
TD-AAS	Thermal decomposition atomic absorption spectrometry
TDS	Total dissolved solids
TOC	Total organic carbon
TV	Threshold value
U	Expanded uncertainty
Uf	Maximum expanded uncertainty
UV-PVG	Ultraviolet photochemical vapour genearation
VOC	Volatile organic compound
XRD	X-ray diffraction
XRF	X-ray fluorescence

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I dedicate this thesis to my family who has always been there for me with an unconditional support.

INTRODUCTION

Research motivation

Based on inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS), the currently used laboratory instrumentation can be distinguished by its good analytical performance characterized by extremely low limit of detection and capability of multi-elemental analysis, simultaneous in case of some methods like ICP-OES and ICP-MS. However, the acquisition price and maintenance of these instruments with large dimensions are expensive and many reagents and samples are needed to be used while performing the analyses. Also, the preparation procedures of the samples are complicated, time-consuming and involve expensive reagents. Considering the above mentioned aspects, the majority of the instrumentations and procedures do not satisfy the requirements of the analytical eco-scale of the Green Analytical Chemistry, proposed by the Polish professor Namiesnik, after 2000. The technology of microplasmas was developed after 2000, as alternative for the clasical laboratory instrumentation. Even if in 2004 the microplasmas were treated with disbelief and considered as toys or curiosities for the academic and research spectroscopic community, nowadays this emergent technology is developing due to the following reasons: (1) microplasmas show unique characteristics by the low operating power of the order of W or even mW and low consumption of Ar or He as support gas of the order of ml min^{-1}, in comparison with the clasical plasmas e.g., operating power higher than 1000 W and gas consumption of 10 – 20 l min^{-1} in case of ICP; (2) the emission spectrum of the elements is simple, therefore low-resolution microspectrometers can be used, powered through the USB port of a calculator, which are sold by companies already existing on the market since several years. Although the problem of the miniaturized spectral instrumentation of detection was solved, the sample introduction into the microplasma and the widening of the analytical applications are still a challenge because of the low operating power of the microplasmas and the limited excitation capacity in presence of solvents. The coupling of the microplasma technology with the green technologies of derivatization of chemical species which use biodegradable organic acids with low molecular weight and more efficient and friendly forms of energy towards the environment e.g., ultrasounds and microwaves, and with the

simultaneous multi-elemental analysis performed directly from liquid samples, are considered revolutionary approaches of the green atomic spectrometry. Therefore, the topic of the present PhD thesis shows a deep innovative character and is indeed in line with international trends in this field. According to this topic, the purposes of the PhD thesis are the confirmation of the analytical competence of a capacitively coupled plasma microtorch with low operating power and low argon consumption, operated at atmospheric pressure, and the development of multi-elemental analytical technologies (some of them simultaneous, among them also the priority hazardous elements such as Cd, Pb, Hg) in order to reach the analytical performance corresponding to the European legislation regarding the determination of pollutants in foods and environment, as alternatives for the clasical ICP-OES, GFAAS instrumentations, thermal decomposition atomic absorption spectrometry (TD-AAS) and atomic fluorescence spectrometry (AFS). It was intended to expand the area of applicability of the miniaturized instrumentation with microplasma source and to solve the problem of the liquid sample introduction in the microplasma by electrothermal vaporization of the microsamples from a Rh filament, in order to perform simultaneous multi-elemental analyses for an increased number of elements of interest for the environment and foods.

Objectives and research metodology

According to state-of+the-art at international level in the domain of atomic spectrometry wit microplasma source, the main objective of the present PhD thesis was the development of a novel modular, fully miniaturized analytical instrumentation, based on capacitively coupled plasma microtorch optical emission spectrometry, with low operating power and low argon consumption, and the development of analytical technologies for such an instumentation which should satisfy the analytical requirements imposed for the determination of pollutants in authorized laboratories, according to the legislation established by the European Committee (Decisions 2002/657/EC, 2007/333/EC and 2011/836/EU).

The specific objectives of the thesis are the following:

1. Development of simultaneous multi-element methods based on a miniaturized system: capacitively coupled plasma microtorch optical emission spectrometry and electrothermal vaporization with rhodium filament (SSETV-μCCP-OES);
2. Development of mercury determination method from food samples based on cold vapour generation and detection by capacitively coupled plasma microtorch optical emission spectrometry (CV-μCCP-OES): analytical characterization and comparison with the requirements of the European legislation;

3. Development of mercury determination method based on sono-induced cold vapour generation and detection by capacitively coupled plasma microtorch optical emission spectrometry (SICV-µCCP-OES): analytical characterization and comparison with atomic fluorescence spectrometry;
4. Study of arsenic beavior and chemical modeling of groundwater from the Banat Plain, southwestern Romania, based on arsenic speciation and co-occuring species in the groundwater, by combining unsupervised multivariate statistical with diagrams.

In order to achieve these goals, the following research methodology was proposed:

1. Development of an experimental model and an SSETV-µCCP-OES prototype for simultaneous multi-elemental determinations from electrothermally evaporated liquid microsamples;
2. Development of modules used for the introduction of microsamples and *on-line* preconcentration of mercury vapours in order to improve the limit of detection;
3. Demonstration of the multi-elemental excitation capacity of the capacitively coupled plasma microtorch from electrothermally evaporated liquid microsamples;
4. Conducting perfomance studies by assessment of limit of detection and quantification, precision and accuracy, by analysis of certified reference materials with the purpose of validation of the novel analytical technologies based on SSETV-µCCP-OES for simultaneous multi-elemental determinations from food and soil samples and comparison with the traditional ICP-OES and GFAAS analytical methods;
5. Conducting perfomance studies by assessment of LOD and LOQ, precision and accuracy, by analysis of C for validation of the novel analytical technologies based on CV-µCCP-OES and SICV-µCCP-OES for mercury determination from foods and comparison with the requirements of the 2002/657/EC, 2007/333/EC and 2011/836/EU European Committee Decisions for authorized quality control laboratories regarding mercury determination from foods, and comparison with the traditional CV-AFS and TD-AAS methods;
6. Implementation of the novel SSETV-µCCP-OES analytical technology for Cd determination from foods and multi-elemental determination (As, Ag, Cd, Cu, Hg, Sb, Sn, Pb and Zn) from environmental samples as alternative of ICP-OES;
7. Implementation of the novel CV-µCCP-OES and SICV-µCCP-OES analytical technologies for Hg determination from foods with and without preconcentration, as alternatives of the traditional TD-AAS and CV-AFS methods, standardized and used in food quality control laboratories;
8. Characterization of groundwater from Banat Plain by speciation of inorganic arsenic (As(III) and As(V)) based on hydride generation and detection by capacitively coupled

plasma microtorch optical emission spectrometry (HG-μCCP-OES), cation (Na^+, K^+, Ca^{2+}, Mg^{2+}) content determined by μCCP-OES with pneumatic nebulization, anion (Cl^-, F^-, SO_4^{2-}, NO_3^-, PO_4^{3-}) content determined by ion chromatography, HCO_3^- content determined by acid-base titration, and determination of pH, redox potential (E_h), electrical conductivity (EC) and total dissolved solids (TDS);

9. Elaboration of a conceptual chemical model for the description of occurance and enrichment of As and other analyzed species in the groundwater bodies from the Banat Plain based on As speciation, hydrogeochemical and mineralogical analysis of rocks from aquifer, Gibbs and Piper diagrams, Stuyfzand hydrogeochemical classification system and unsupervised chemometric approaches (principal component analysis – PCA, fuzzy principal component analysis – FPCA and fuzzy hierarchical cross-clustering – FHCC).
10. Copyright protection of instrumentation and novel analytical technologies.

Scientific presentation of the PhD thesis

The research presented in this PhD thesis was performed within the partner project entitled ***Miniaturized equipment with capacitively coupled plasma microtorch and analytical technologies for simultaneous elemental determination used in environment and food control (MICROCCP), project number PCCA 176/02.07.2012***, coordinator Babeş-Bolyai University of Cluj-Napoca, project director Prof. Dr. Tiberiu Frenţiu, also the scientific advisor of the present PhD thesis.

The thesis is structured in six chapters. Among these chapters, five are dedicated to the experimental part and personal contributions. The bibliographic part contains 381 references. Chapter I contains the theoretical presentation of the emerging technology of microplasmas and their applications. Chapter II presents the development of simultaneous determination methods from food and environmental samples based on the miniaturized SSETV-μCCP-OES instrumentation. Chapter III describes Hg determination methods with clasical derivatization from environmental and food samples using the innovative CV-μCCP-OES instrumentation. Chapter IV presents the development of a Hg determination method based on sono-induced derivatization in formic acid and detection by SICV-μCCP-OES. Chapter V describes the study of As behavior and occurance in the groundwater from Banat Plain by speciation of As under the As(III) and As(V) forms by HG-μCCP-OES method. The last chapter contains the elements of originality of the present research, the novel contributions in this research domain and the general conclusions.

THEORETICAL PART

CHAPTER I. MICROPLASMA TECHNOLOGY APPLIED IN SPECTROMETRY

Plasma is considered the fourth state of matter and it consists of an almost neutral mixture of electrons, positive and negative ions, atoms and molecules, as results of matter ionization. The analytical plasma is obtained by ionization of a support gas (Ar, He, N_2, H_2, CH_4 or gas mixtures), by the interaction with a direct or alternative electric field, in a special device called torch [1]. The emergent microplasma technology and the related instrumentation started its development since 2000. Even if in 2004 the microplasmas were considered as toys by researchers, nowadays they represent a dynamic field in the green analytical chemistry with applicability in the atomic spectrometry. The microplasma sources present interesting characteristics by their low power consumption of the order of mW or W and low argon or helium consumption as gas support of the order of ml min^{-1}, as well as the simple emission spectrum of elements which mainly contains resonance lines, therefore they can be interfaced with low resolution microspectrometers without spectral interferences [2]. As the microplasma sources can be powered by accumulators and batteries, whereas the microspectrometers by the USB port, as result of these advantages, they represent the main pieces of a portable instrumentation with a working power up to even 24 hours. The microplasma sources benefit from the instrumental technologic progress and the principles of GAC concerning sample preparation, derivatization technologies, etc. [3,4]. Even if initially it was considered that the microplasma and the corresponding device (microtorch) should have a smaller dimension than 100 μm, this definition was reconsidered and expanded to devices with dimensions in the order of mm or cm, if the devices are microfabricated. All plasma sources were miniaturized but some of them were imposed in fundamental and applicative research [2].

Direct current microplasma. There are two important direct current microplasmas: 1. Direct current planar microplasma and 2. microplasma or microhollow cathode discharge (MHCD), known also as micro-structured electrode (MSE) discharge [5.6]. Plasmas in quartz capillaries were also developed [7]. The main applications of direct current microplasmas are methane detectors [8], specific detectors used in gas chromatography of halogenated volatile organic compounds (VOCs) [7,9], and ionization sources used in mass spectrometry coupled with gas chromatography, at the absolute limit of detection in the order of pg [10].

Postage-stamp sized alternative-flow microplasma cip (MDP). This microplasma type is developed in mixtures of Ar – H_2 and He – H_2 (220 – 250 ml min^{-1}, 4 – 5 W power) on a

hybrid device for liquid elemental analysis by electrothermal vaporization (40 W) and optical emission spectrometry (ETV-MPD-OES) with detection limits of 5 – 350 pg [11-14]. The scheme of the experimental set-up is depicted in Fig. 1.1 [11,12].

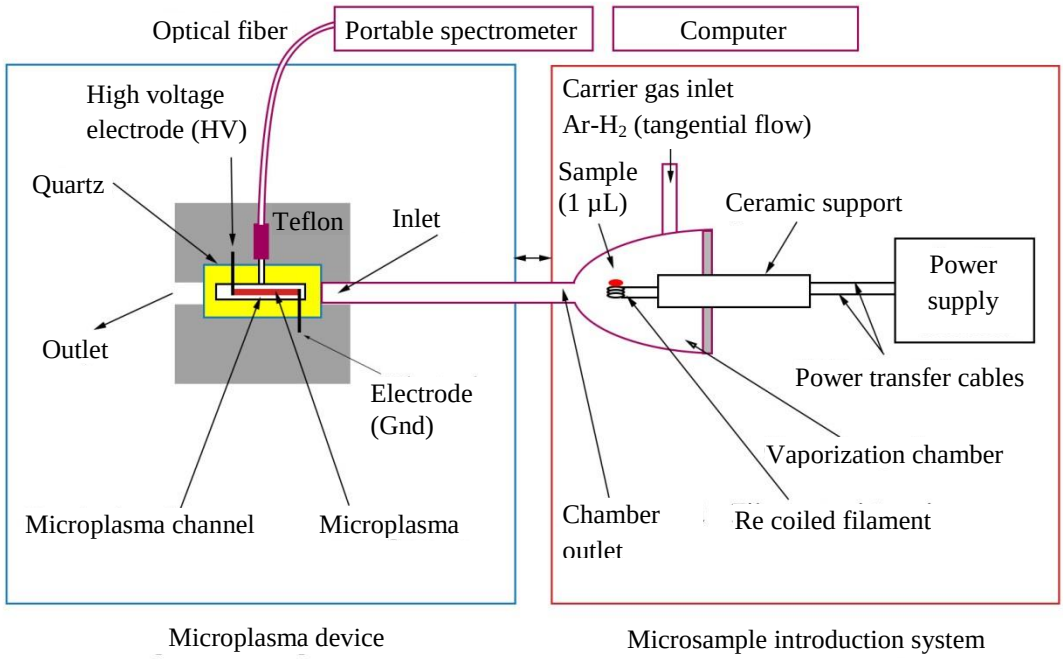

Fig. 1.1. Scheme of ETV-MPD-OES experimental set-up for simultaneous determination of elements with a microspectrometer with CCD and optical fiber from electrothermally evaporated liquid microsamples [11,12].

Microfabricated inductively coupled plasma (mICP). This microplasma was developed by Hopwood *et al*. [15-17] in a glass chamber by coupling radio frequency electrical energy (0.5 – 20 W, frequency 460 and 818 MHz) under vacuum (0.1 – 10 torr) in Ar, air or He atmosphere, by a Cu-coil deposition on the wall of the chamber under vacuum. By approaching the coil to the plasma and increasing the frequency to 818 MHz, the mICP discharge could be developed even at atmospheric pressure, at a power of only 1 W and gas consumtion of only 0.7 ml min^{-1}, as an excellent SO_2 detector at the S 469.5 nm emission line and limit of detection of 45 µg l^{-1} [17].

Ichiki *et al.* [18] investigated a mICP jet (power 50 W, frequency 144 – 146 MHz, Ar consumption 0.7 l min^{-1}), as source in the AES for determination of elements from liquid samples but the limits of detection were too poorer for analytical applications (5 µg ml^{-1} Na).

Capacitively coupled microplasma. In case of capacitively coupled plasma the radio frequncy power is coupled by electrodes and at least one electrode is in contact with the plasma. According to the arrangement of the electrodes, there are three clasical coupling

geometries, presented in Fig. 1.2: 1. With annular electrodes; 2. With parallel plane (PP) electrodes; 3. With axial electrode(s) [19].

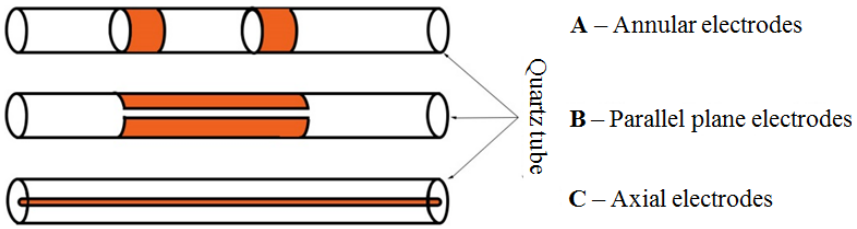

Fig. 1.2. Configurations of electrodes in case of rfCCP plasma torches [19].

The first miniaturized capacitively coupled plasma torch with parallel plane (PP) electrodes (PP-CCP) presented in Fig. 1.3, was developed by Professor Blades and coworkers at British Columbia University, Vancouver, Canada, but no analytical applications were applied [20].

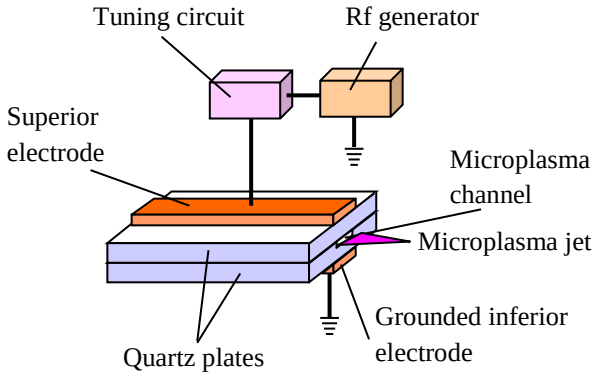

Fig. 1.3. Scheme of the capacitively coupled plasma torch with parallel plane electrodes (PP-CCμP) developed on a quartz glass chip [20].

A similar alternative of the capacitively coupled microplasma (1 – 5 W, frequency 13.56 MHz) with parallel plane electrodes (CCMP), was prposed by Yoshiki and Horiike [21] as specific emission detector for gas chromatography. Brede *et al.*, [22-24], interfaced a capacitively coupled microplasma with annular geometry (0.5 – 2 W, He flow only 1 – 3 ml min^{-1} and O_2 or H_2 flow only 0.15 – 1.5 ml min^{-1}) with a gas chromatograph, as ionization source in mass spectrometry for VOCs with F, Cl, Br and I, and speciation of organotin compounds (GC-CCμP-MS). Guchardi and Hauser [25-27] investigated the analytical capacities of a capacitively coupled microplasma (8 W, 20 kHz, 3 – 200 ml min^{-1}, Ar or He) with annular geometry, developed in a quartz capillary with inner diameter of 250 μm and outer diameter of 350 μm for determination of As, Sb and Hg by chemical vapour generation, as gas detector with emission in Vis-IR and detector for gas chromatography of VOCs. The research group of Professor Platzer from Graz University, Austria developed a stabilized

capacitive microplasma (SCP) which was used afterwards by the Anton Paar GmbH company from Graz as specific atomic emission detector in gas chromatography (GC-μ-AED) of polychlorinated compounds based on carbon and chlorine emission [28].

Dielectric barrier discharge microplasma (DBD). Conceptually, DBD is charachterized by the presence of at least one layer of dielectric (barrier) quartz, ceramic or polymeric material, with a thickness of 0.1 – 10 mm between the two electrodes which are subjected to an alternative low/high voltage electric field, with low square, sinusoidal or pulsed wave frequency [2]. The advantage of the DBD coupling can be described by the fact that there is no contact between the plasma and the electrodes, therefore the impurification of the plasma and the damage of electrodes by cathodic sputtering is excluded. Its use as multi-element detector in gas chromatography (GC-DBD-OES) is one of the remarkable applications, based on a DBD Ar plasma at atmospheric pressure and a portable CCD microspectrometer, applied with succes by Hou and coworkers [29] for determination of halogenated hydrocarbons separated on GC column with limit of detection of 0.02 – 0.3 μg ml^{-1} per element. Jiang *et al.* [30] investigated the analysis of liquid microsamples by the ETV-DBD-OES compact coupling presented in Fig. 1.4, equipped with a CCD microspectrometer and a miniaturized electrothermal evaporator with W filament, for the introduction of a liquid microsample of volume of 10 μl by vaporization from the filament, obtaining limits of detection of 0.8 μg l^{-1} in case of Cd and 24 μg l^{-1} for Zn. Li *et al*. [31] demonstrated the efficient multi-elemental atomization and excitation capacity of DBD with limits of detection of 0.16 – 11.65 μg l^{-1} for the simultaneous determination of Hg, Zn, Pb, Ag, Cd, Mn, Fe, Cr and As from liquid microsamples subjected to electrothermal vaporization from W filament.

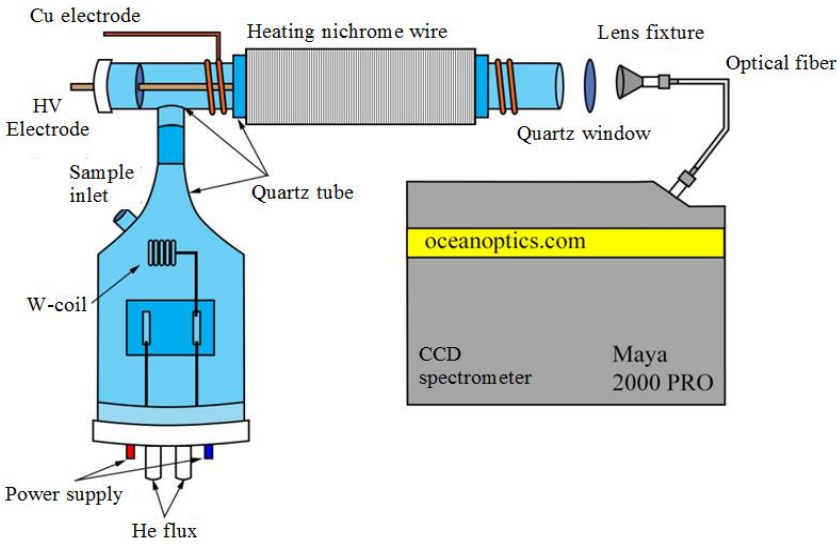

Fig. 1.4. Schematic diagram of the ETV-DBD-OES instrumental set-up used for simultaneous multi-elemental analysis of liquid microsamples vaporized from a W filament [30].

Microwave microstrip plasma (MSP). The miniaturization of the microwave plasma (5 – 50 W, 2.45 GHz, 0.25 – 1 l min^{-1} Ar or He) on a quartz chip and its analytical application for determination of chemical vapour generating elements (Hg, As, Sb) and detector of VOCs was developed by the research group of Professor Broekaert from Germany [32-38]. Feng *et al*. [39] investigated a miniaturized simultaneous spectrometer equipped with a microwave plasma torch (MPT) for determination of elements from aqueous solutions, introduced by pneumatic nebulization with aerosol drying, with LOD between 0.58 and 48.8 ng ml^{-1}.

Liquid electrode microplasma. This microdischarge is unique by the fact that the plasma is developed as electrod on the surface of the liquid sample while the sample gets into the plasma by sputtering cauzed by the action of the electric particles (Ar or He ions and electrons). This was evidenced by Cservalfi *et al.* [40]. According to the nature of the sample, cathode or anode, the liquid electrode plasma is called flowing liquid cathode (FLC-APGD) or flowing liquid anode atmospheric pressure glow discarge (FLA-APGD) [41-45] (Fig. 1.5).

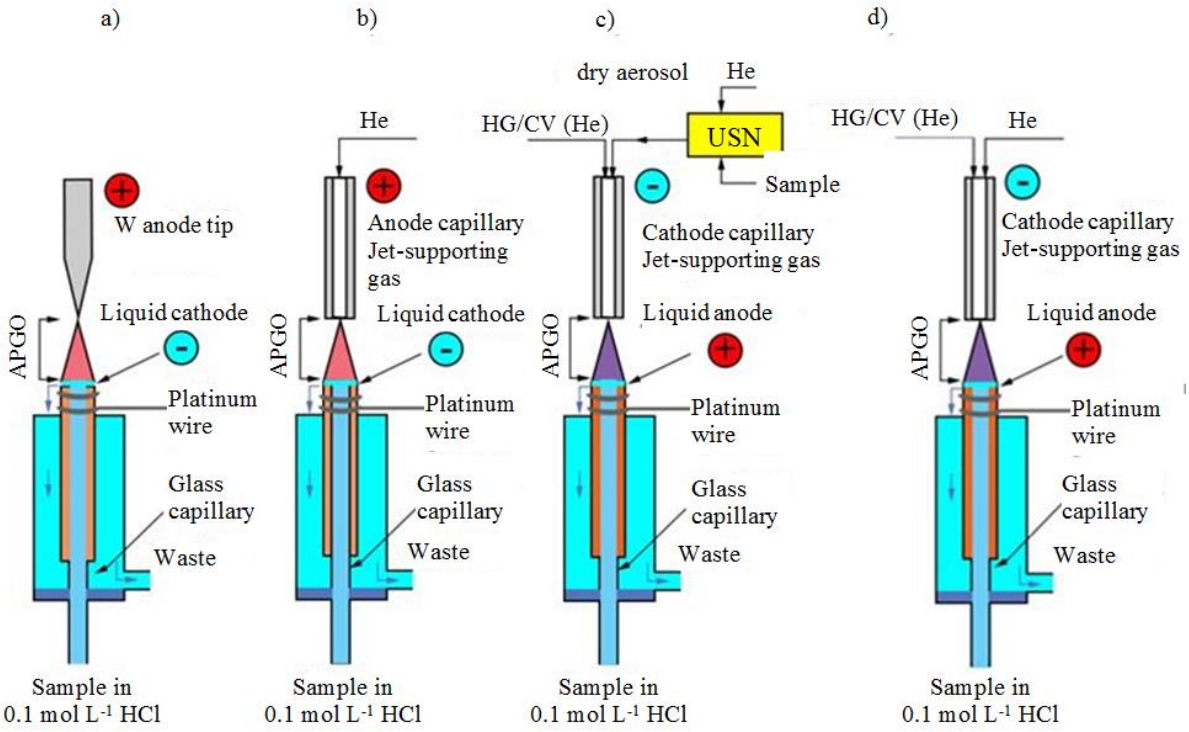

Fig. 1.5. Classical FLC-APGD coupling with capillary cathode and anode tip with discharge in open air (a), capillary anode in He inert atmosphere (b) and FLA-APGD coupling with capillary anode and cathode tip with discharge in He inert atmosphere (c) capillary cathode in He inert atmosphere (d) used for direct analysis of liquid samples [43-45].

The main characteristics of the liquid electrode microplasma, its applications and analytical performance for multi-elemental determinations by optical emission spectrometry were recently described [41]. FLA shows good LODs just for a limited set of elements [44].

PERSONAL CONTRIBUTIONS

CHAPTER II. SIMULTANEOUS MULTI-ELEMENT METHODS BASED ON A MINIATURIZED SYSTEM: CAPACITIVELY COUPLED PLASMA MICROTORCH OPTICAL EMISSION SPECTROMETRY AND ELECTROTHERMAL VAPORIZATION WITH RHODIUM FILAMENT

2.1. Situation at international level. Working hypothesis and objectives

The miniaturization of the spectral intrumentation for the UV-Vis domain is one of the representative research fields in the modern analytical chemistry, regarding devices for sample preparation and introduction in plasma, spectral atomization, excitation and ionization sources and detection systems [46]. The introduction of the liquid sample in the microplasma is problematic because of the low tolerance towards water, as a result of the low operating power. Therefore, the stability of the discharge is highly influenced by the presence of solvents. This characteristic limits the analytical applications of microplasma sources in spectrometry in case of direct analysis from liquid samples introduced by pneumatic or ultrasonic nebulization [47,48]. The coupling concept between a miniaturized electrothermic evaporator as device for liquid sample introduction and a source of a He/Ar-H_2 portable microplasma charged with a battery and detection by optical emission spectrometry (ETV-MPD-OES) was the result of pioneer research conducted in the school of Karanassios in Canada [11,13,14]. This approach allowed the extension of the analytical applications of microplasmas for simultaneous multi-elemental analyses in case of volatile elements with resonance lines with excitation energies up to 7 eV, from micro- and nanovolumes of sample, with limits of detection at ng ml^{-1} level or absolute level of pg. The research objectives of the present PhD thesis were: 1. Development of novel miniaturized instrumentation composed of miniaturized devices for electrothermal vaporization and a low power and low Ar consumption capacitively coupled plasma microtorch and detection by optical emission spectrometry with low rezolution microspectrometers (SSETV-μCCP-OES); 2. Development of simultaneous multi-elemental methods with applications in food and environment quality control also for the determination of priority hazardous elements (Cd, Pb, Hg) which do not own reported literature studies. The novelty and originality of the present study consists of the development of a fully miniaturized analytical system and its implementation as laboratory equipment and expansion of its versatile applications for areas of interest, such as food and

environment quality control by determination of representative elements from such samples, as sustainable alternative for the ICP-OES and GFAAS instrumentation and methods.

2.2. Fully miniaturized SSETV-µCCP-OES instrumentation

A fully miniaturized SSETV-µCCP-OES analytical system (OSIM patent granted) for laboratory use was developed [49-53] (Fig. 2.1).

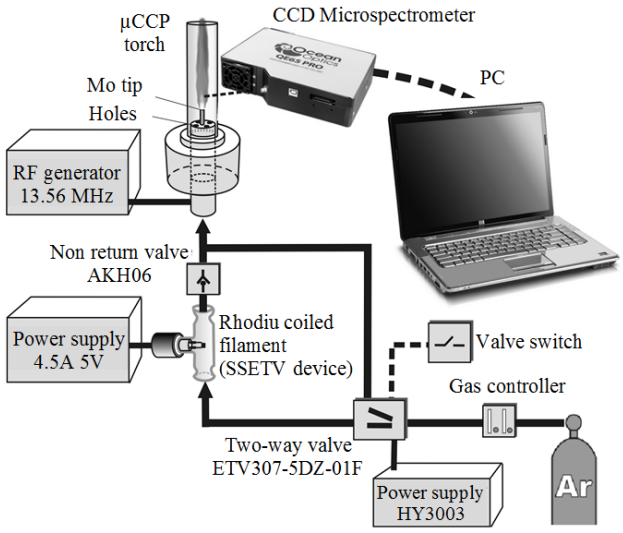

Fig. 2.1. Schematic diagram of the SSETV-µCCP-OES prototype model [52].

The SSETV-µCCP-OES prototype analytical system is composed of a miniatirized electrothermal evaporator with Rh filament (Babeş-Bolyai University, Cluj-Napoca, Romania), manually controlled by HM 7042-6 (Hameg Instruments, Mainhausen, Germany) or a power source automatically controlled by a software (Technical University, Cluj-Napoca, Romania), a capacitively coupled plasma microtorch with Mo tip microelectrode (INCDO-2000, Bucharest, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania), a miniaturized free-running radio frequency generator 13.56 MHz, 15x17x24 cm^3 (Technical University, Cluj-Napoca, Romania), a HY3003 Mastech, Premier Farnell (Leeds, UK) continuous power source for the control of the two way standard valve SMC EVT307-5DZ-01F-Q, Premier Farnell (Leeds, UK), an Ocean Optics QE65 Pro (Dunedin, USA) microspectrometer with 190 – 380 nm spectral range, Full Width at Half Maximim (FWHM 0.4 nm), equipped with a Hamamatsu S7031-10065 coupled charge detector (CCD), cooled at -20 ºC [52].

A scheme of the µCCP microtorch and the miniaturized electrothermal evaporator is depicted in Fig. 2.2 [49,50].

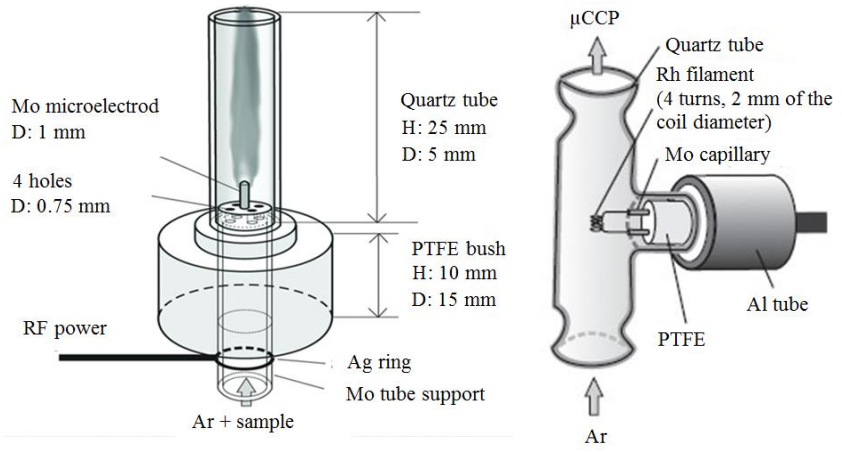

Fig. 2.2. Construction details of the capacitively coupled plasma microtorch and the miniaturized electrothermal evaporator [49,50].

The plasma microtorch consists of a Mo microelectrode with 1 mm diameter (Goodfellow, Cambridge, UK), fitted in a PTFE support and a quartz tube with 5 mm diameter, 25 mm length and 160 nm limit cutting (H. Baumbach & Co Ltd. Ipswich Suffolk, UK). An argon flux with a flow rate of 50 – 200 ml min^{-1} was used for the discharge support and sample transport in the plasma. The argon and the sample enter together into the plasma through four holes with diameters of 75 µm, made in the PTFE support, on a circle with 3 mm diameter around the Mo tip microelectrode. The low power plasma (10 – 30 W) appears as blue luminescent discharge at the tip of the microelectrode, connected to the miniaturized radi frequency generator [49,50]. The emission spectrum was recorded on a spectral range of 190 – 380 nm with the QE65 Pro microspectrometer, charged by the USB port of the laptop. The QE65 Pro microspectrometer was equipped with a back-illuminated Hamamatsu CCD detector, cooled at -20 ºC, which resulted the improvement of limits of detection because of the high signal-to-background ratio. The electrothermal evaporator [49,50] consists of a vaporization chamber formed by T-shaped quartz tubes, with a volume of cm^3, the spiral Rh filament being fitted in its interior. The 99.9% purity Rh filament was thermally treated by the manufacturer (Goodfellow, Cambridge, UK). The use of the thermally treated Rh filament is advantageous because it is slightly malleable and workable and allows the performing of at least 2500 – 3000 thermal cycles, without its demage. Nevertheless, Rh is an almost chemically inert metal against nitric acid or *aqua regia,* and does not retain oxygen, therefore the use of hydrogen is not necessary that increase the spectral background signal in UV.

2.3. Operation of the SSETV-µCCP-OES analytical system. Characteristics of the multi-elemental emission spectrum

The analytical system was operated by drying 10 µl sample on the Rh filament at 100ºC, vaporization of the dried sample at 1500ºC and recording 20 episode spectra (Fig. 2.3). [50-53].

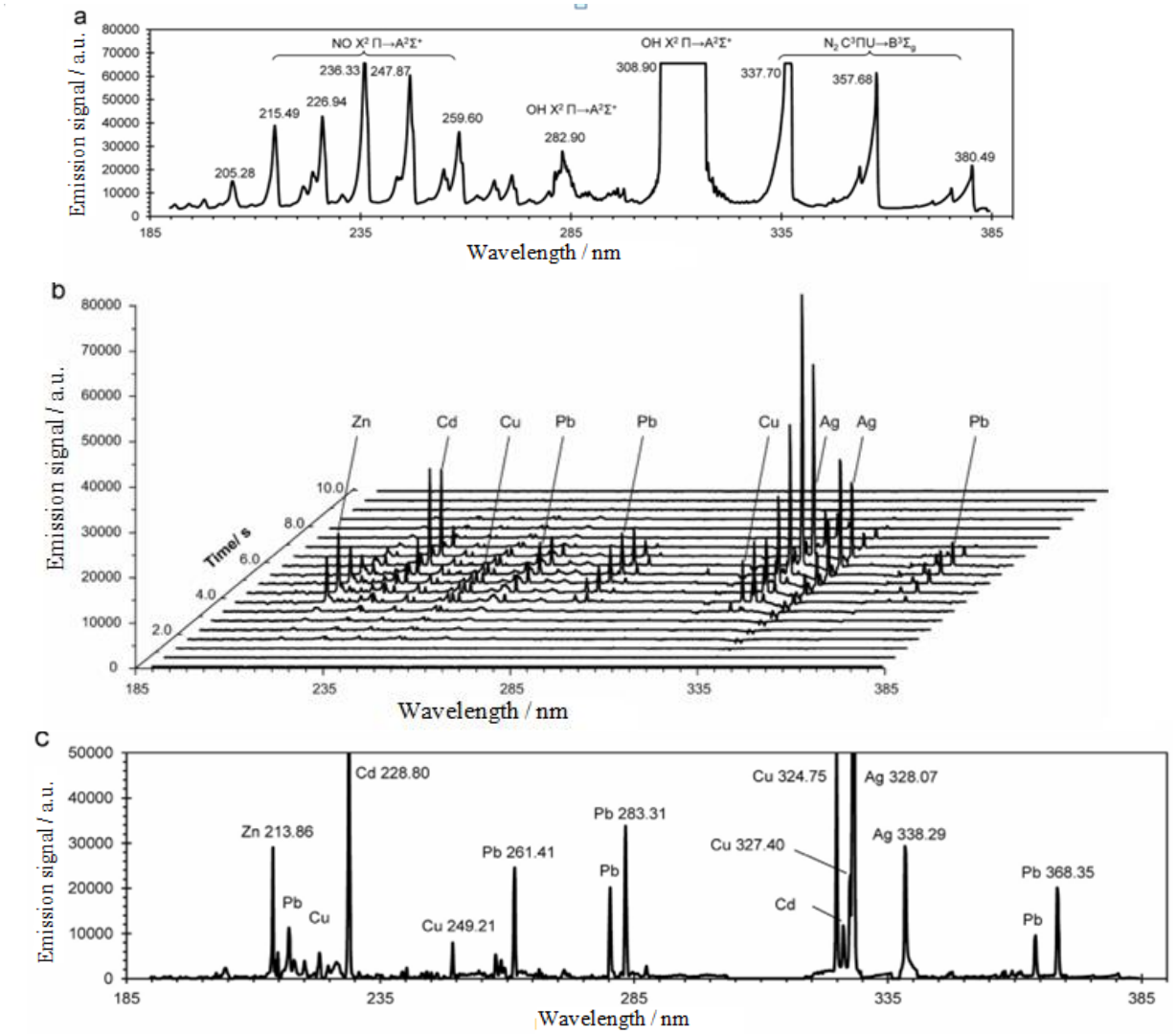

Fig. 2.3. (a) Background emission spectrum of Ar µCCP; (b) Net episode spectra recorded by the SSETV-µCCP-OES method for a multi-element solution of 50 ng ml^{-1} Ag, Cd, Zn; 200 ng ml^{-1} Cu, 500 ng ml^{-1} Pb; (c) Total emission spectrum obtained by summation of episode spectra. Measurement conditions: plasma power 15 W; Ar flow 150 ml min^{-1}; plasma observation height 0.8 mm; integration time per episode 500 ms (20 spectra) [50].

The emission spectrum is simple, formed by resonance and non-resonance atomic lines with excitation energy at most 7 eV, therefore a low resolution microspectrometer (FWHM 0.4 nm) could be used.

2.4. Determination of Cd from food samples by SSETV-µCCP-OES: comparison with the GFAAS method and the requirements of the European legistation

The analyzed samples were liophilized and mineralized in 60% HNO_3 and 2 ml 30% H_2O_2 in PTFE vessels, in a microwave digestion system [54]. The optimal working conditions for Cd determination from foods by the SSETV-µCCP-OES are presented in Table 2.1 [52].

Table 2.1. Optimal working conditions for Cd determination from food samples by the SSETV-µCCP-OES method [52].

Electrothermal vaporization device with Rh filament	
Microsample volume	10 µl
Standard addition calibration	0 – 8 ng ml^{-1} Cd (5 additions)
Microsample drying	Temperature 100 ºC; Drying time 80 s; Voltage 0.26 V; Electric power intensity 2.11 A
Microsample vaporization	Temperature 1500 ºC; Vaporization time 6 s; Voltage 2.2 V; Electric power intensity 4.77 A
Rh filament temperature control	Controlled by software by applied voltage; Temperature control precision 5% [55]
Matrix modifier	No
Plasma microtorch	
Power	15 W
Ar flow	150 ml min^{-1}
Plasma viewing	0.8 mm above top microelectrode
QE65 Pro microspectrometer	
Spectra recording mode	Episode spectra (High Speed Acquisition)
Number of episode spectra	20
Integration time/episode	500 ms
Signal processing	Peak height at 228.802 nm
Detector temperature	- 20 ºC Peltier cooler

The SSETV-µCCP-OES method was validated regarding the imposed requirements for the analytical methods used in authorized quality control laboratories [56-60]. The considered parameters for validation were: LOD, LOQ, precision, accuracy and specificity. The obtained results by SSETV-µCCP-OES method were compared with the ones determined by GFAAS, using the Bland and Altman statistical test [58-62]. The experimental measurements demonstrated that the SSETV-µCCP-OES method is affected by non-spectral interferences of the multi-mineral matrix, which were successfully compensated by the standard addition method. The parameters of the calibration curves and limits of detection obtained by the SSETV-µCCP-OES method using standard addition are presented in Table 2.2 [52].

According to Table 2.2, the found limits of detection by SSETV-µCCP-OES method for three CRM samples are similar, in the range of 0.009±0.001 mg kg^{-1} Cd in liophilized

samples. In case of GFAAS method, LOD was 0.006 mg kg^{-1} Cd and 0.012 mg kg^{-1} Cd. The LOD and LOQ values in fresh foods, calculated for the two methods and compared with the maximum levels (ML) [52] for different food categories demonstrate that the SSETV-μCCP-OES method satisfies the requirements of the European Committee regarding Cd determination because LOD and LOQ values are 15 – 160, respectively 8 – 80 times lower than the ML values of the analyzed foods [57]. The limits of detection and quantification obtained by SSETV-μCCP-OES method are similar with those obtained by GFAAS method, and also similar with those reported for other microplasma sources [30,50,63-68]. Table 2.3 shows that the SSETV-μCCP-OES method assures recovery in the range 88–118% in case of CRM sample analyses, similar with the ones obtained with the GFAAS method (101±8%) if standard addition is used for the compensation of matrix effects [53]. The trueness of the method is (-3)-(+7.3)%. The SSETV-μCCP-OES method satisfies the requirements of the European Committee regarding Cd determination from foods [59].

Table 2.4 presents the measurement results of the repeatability study conducted on food test samples [52]. The determination precision by SSETV-μCCP-OES was in the interval of 4.0 – 14.0% for Cd concentrations below MLs and between 0.8 – 6.0% for Cd concentrations near or above MLs. The proposed method satisfies the requirements of the 2007/333/EC decision concerning precision: the HorRat index <2 and the measurement uncertainty U<Uf [59]. The precision of the SSETV-μCCP-OES method is similar with the precision of GFAAS (0.6 – 10.0%). The Bland and Altman test showed that there are no significant differences between the mean results obtained by the two methods at 95% confidence level [52].

2.5. Simultaneous multi-elemental determination from soil samples by SSETV-μCCP-OES: comparison with the ICP-OES method

The SSETV-μCCP-OES method was verified by ICP-OES method, using the SPECTRO CIROS^{CCD} (Spectro, Kleve, Germania) instrument. The description of the instrumentation and working conditions are presented in Table 2.5 [53]. Table 2.5 includes the limits of detection for liquids and solids obtained by the SSETV-μCCP-OES method in comparison with the ICP-OES method [53]. This table also presents the normal values of elements in soil, according to HG 756/1997 [68]. In case of SSETV-μCCP-OES compared with ICP-OES, the limits of detection show better values for elements with lower excitation energy (Ag, Cu, Pb and Zn), similar values for Hg, Sb, Sn and lower values for elements with higher excitation energy (As and Cd). Mercury can be determined only at higher concentrations than 1 mg kg^{-1}, value which corresponds to the alert limit of sensible soils, according to HG 756/1997 [68].

Table 2.2. Calibration curve parameters, limits of detection and quantification in case of Cd determination obtained by SSETV-μCCP-OES using standard addition in liophilized CRM samples [52].

CRM	Slope (m) (ml ng^{-1})	Y-intercept	r	$s_{y/x}$	LOD (ng ml^{-1})	LOD (mg kg^{-1})	LOQ (mg kg^{-1})
IC-CS-CR-2	291	1081	0.9994	32	0.33	0.010	0.020
BCR-185R	258	1103	0.9995	22	0.25	0.008	0.015
IAEA-359	238	313	0.9991	25	0.38	0.010	0.019
Mean value			0.9993±0.0002		0.32±0.07	0.009±0.001	0.018±0.003

Table 2.3. Cd determination results obtained for some certified reference materials analyzed by SSETV-μCCP-OES and GFAAS [233].

Certified reference material	Certified value±U[a] (mg kg^{-1})	Found value±U[a,b] (mg kg^{-1})		Recovery (%)	
		SSETV-μCCP-OES	GFAAS	SSETV-μCCP-OES	GFAAS
IC-CS-CR-2	0.196[c]	0.210±0.018	0.203±0.008	107±8	104±4
BCR-185r	0.544±0.017	0.552±0.031	0.555±0.030	101±6	102±5
IRMM-804	1.61±0.07	1.71±0.15	1.57±0.09	106±9	97±6
IAEA-359	0.12±0.05	0.13±0.03	0.13±0.01	107±25	108±8
DOLT-4	24.3±0.8	24.4±1.6	24.6±0.6	100±6	101±3
TORT-2	26.7±0.6	25.9±2.2	26.0±0.8	97±8	97±3
BCR-191	0.0284±0.0014	0.0289±0.0032	0.0271±0.0018	102±11	95±7
NIM-GBW10011	0.0184±0.004	0.019±0.005	0.019±0.003	105±26	105±16
Average recovery (%)[b]				**103±15**	**101±8**

a-expanded uncertainty
b-expanded uncertainty for 95% confidence level (n=5 replicates)
c-indicative value

Table 2.4. Obtained results (mg kg^{-1}) for Cd determination in food test samples by SSETV-μCCP-OES and GFAAS (n=5) [52].

Sample	GFAAS		SSETV-μCCP-OES					
	Mean (mg kg^{-1})	u (mg kg^{-1})	Mean (mg kg^{-1})	u (mg kg^{-1})	RSD (%)	PRSD (%)	Hor Rat ratio	U_f
Soy	0.015	0.001	0.015	0.001	6.7	29.8	0.22	0.005
Potato 1	0.199	0.020	0.205	0.020	9.8	20.1	0.49	0.037
Potato 2	0.219	0.005	0.219	0.006	2.7	20.0	0.14	0.039
Mushroom 1	0.494	0.015	0.485	0.030	6.2	17.7	0.35	0.087
Mushroom 2	0.648	0.004	0.656	0.008	1.2	16.9	0.07	0.098
Spinach	0.759	0.022	0.747	0.039	5.2	16.6	0.31	0.112
Salad	0.743	0.009	0.765	0.006	0.8	16.5	0.05	0.115
Wheat flower 1	0.040	0.002	0.044	0.002	4.5	25.4	0.18	0.010
Wheat flower 2	0.020	0.002	0.019	0.002	10.5	28.8	0.36	0.006
Bran	0.180	0.004	0.192	0.002	1.0	20.3	0.05	0.035
Vegetal cheese	0.026	0.001	0.026	0.001	3.8	27.5	0.14	0.005
Chicken liver 1	0.155	0.004	0.159	0.008	5.0	20.9	0.24	0.029
Chicken liver 2	0.165	0.006	0.161	0.005	3.1	20.9	0.15	0.029
Pork liver pate	0.079	0.005	0.079	0.011	14.0	23.2	0.60	0.016
Pork fillet	0.048	0.003	0.054	0.003	5.6	24.6	0.23	0.011
Chicken meat	0.040	0.001	0.040	0.001	2.5	25.7	0.10	0.008
Carp fillet	0.025	0.002	0.023	0.003	13.0	28.0	0.46	0.005

The result obtained in the accuracy study showed that the values obtained by SSETV-μCCP-OES are consistent with the the certified values and the ones obtained by ICP-OES (Table 2.6) [53]. Tables 2.7 and 2.8 present the results of the analysis of some soil test samples by SSETV-μCCP-OES and ICP-OES methods [53]. The statistical tests (t) and (F) indicated that the mean results and the measurement precision obtained by the SSETV-μCCP-OES method are similar with the ones obtained by the standard ICP-OES method at 95% confidence level [53].

Table 2.5. Limits of detection for the simultaneous multi-elemental analysis of soil microsamples by SSETV-μCCP-OES and ICP-OES, in comparison with the normal values in soil [53].

Ele-ment	λ/nm	E_{ex}/ eV	Calibration domain/ μg ml^{-1}	SSETV-μCCP-OES						ICP-OES[a]			Normal value in soil/ mg kg^{-1}[f]
				Correlation coefficient (r)	*RSDB*/ %[b]	*SBR*[c]	*LOD*/ ng ml^{-1}	*LOD*/ pg[d]	*LOD*/ mg kg^{-1}[e]	Correlation coefficient (r)	*LOD*/ ng ml^{-1}	*LOD*/ mg kg^{-1}[e]	
As	193.759	6.40	0 – 10	0.9998	0.5	0.40	40	400	1.0	1.000	5.0	0.13	5
Ag	328.068	3.78	0 – 10	0.9975	0.3	6.20	1.5	15	0.04	1.000	5.6	0.14	2
Cd	340.365	7.37	0 – 10	0.9990	0.3	0.50	20	200	0.50				1
	214.438									1.000	1.0	0.03	
Cu	324.754	3.81	0 – 10	0.9990	1.5	25	1.8	18	0.05	0.9998	8.2		20
Hg	253.652	4.89	0 – 10	0.9986	0.7	1.40	15	150	0.38	0.9987	15	0.38	0.1
Pb	368.346	4.33	0 – 10	0.9995	0.3	0.45	20	200	0.50				
	220.351									0.9999	35	2.0	20
Sb	217.581	5.69	0 – 10	0.9990	1.6	1.40	34	340	0.85				5
	206.833									0.9990	32	0.80	
Sn	326.233	4.78	0 – 10	0.9990	1.2	8.20	4.4	44	0.11				
	189.991									0.9975	5.8	0.15	20
Zn	213.856	5.80	0 – 10	0.9997	0.7	7.00	3.0	30	0.08	1.000	8.4	0.21	100

[a] – method developed in our laboratory with the CIROSCCD spectrometer with pneumatic nebulization without desolvation

[b] – percent relative standard deviation of background calculate from twenty episode spectra

[c] – signal-background ratio for 1 μg ml^{-1} element concentration

[d] – absolute limit of detection calculated for 10 μl sample volume

[e] – limit of detection calculated for 2 g mineralized sample, diluted to 50 ml

[f] – normal values in soil, according to Romanian legislation (H.G.756/1997) [68]

Table 2.6. Results of soil and sediment CRMs analysis by SSETV-μCCP-OES and ICP-OES (mean±U[a], n=3 parallel measurements) [53].

CRM		Ag	As	Cd	Cu	Hg	Pb	Sb	Sn	Zn
RTC CRM048-050G soil	Certified value	75.2±1.57	123±5.4	140±3.28	277±6.03	28.0±1.13	86.9±2.42	139±13.9	93.5±3.24	724±21.2
	SSETV-μCCP-OES	75.3±0.95	128±6.0	141±5.23	271±8.09	27.0±2.85	89.0±4.40	141±18.0	94.4±6.54	752±26.6
	ICP-OES	75.8±0.87	130±8.0	141±5.75	268±9.05	26.0±3.21	88.9±5.40	126±16.8	98.9±6.32	762±28.1
CRM0025-050 soil	Certified value	-	339±51.1	369±46.3	7.76±1.68	99.8±31.7	1447±203	-	-	51.8±8.29
	SSETV-μCCP-OES	-	345±26.2	353±25.1	9.67±2.90	96.1±23.8	1544±250	-	-	49.9±10.1
	ICP-OES	-	331±25.2	348±22.8	9.85±2.80	113±20.1	1641±222	-	-	58.9±7.20
LGC 6141 soil	Certified value	-	13.2±3.5	-	51.1±13	-	75.8±16	-	-	169±39
	SSETV-μCCP-OES	-	14.2±2.1	-	52.8±6.0	-	76.6±10.1	-	-	175±20
	ICP-OES	-	14.3±2.2		57.5±7.0		67.5±9.1			161±15
BCR-280R lake sediment	Certified value	-	33.4±2.9	0.85±0.10	53±6	1.46±1.20	-	-	9.5±1.7	224±25
	SSETV-μCCP-OES	-	27.7±6.1	0.82±0.20	54±6	1.31±0.35	-	-	9.1±1.9	224±6
	ICP-OES	-	29.1±5.3	0.80±0.20	56±6	1.50±0.25	-	-	8.8±1.9	223±4
ERM-CC141 soil	Certified value	-	7.5±1.4	0.25±0.05	14.4±1.4	-	32.2±1.4	-	-	57±4
	SSETV-μCCP-OES	-	9.0±1.7	<LOD	15.1±2.0	-	33.4±3.5	-	-	55±6
	ICP-OES		7.8±1.2	0.28±0.10	15.4±1.2	-	30.1±2.6	-	-	55±6
LGC 6135 soil	Certified value	-	66±12	-	105±5	3.2±0.4	391±16	-	(35)	316±41
	SSETV-μCCP-OES	-	58±10	-	110±10		396±15	-	35±3	320±30
	ICP-OES	-	65±8	-	118±17	2.9±0.6	406±20	-	37±3	298±20
NCSDC 78301 river sediment	Certified value	-	56±10	2.45±0.3	53±6	0.22±0.04	79±12	-	-	(251)
	SSETV-μCCP-OES	-	53±6	2.20±0.4	63±15	<LOD	84±11	-	-	265±20
	ICP-OES	-	55±6	2.15±0.4	59±7	<LOD	83±6			275±25
BCR-280R lake sediment	Certified value	-	33.4±2.9	0.85±0.10	53±6	1.46±1.20	-	-	9.5±1.7	224±25
	SSETV-μCCP-OES	-	27.7±6.1	0.82±0.20	54±6	1.31±0.35	-	-	9.1±1.9	224±6
	ICP-OES	-	29.1±5.3	0.80±0.20	56±6	1.50±0.25	-	-	8.8±1.9	223±4
Recovery/ % mean±U[a]	SSETV-μCCP-OES	100±2	98±16	96±18	107±16	92±23	104±11	101±13	98±16	101±10
	ICP-OES	101±1	98±14	98±23	111±14	102±17	101±10	91±14	99±16	101±8

[a] U represents the extended uncertainty at 95% confidence level

Table 2.7. Results (mean±U, mg kg^{-1}) obtained by SSETV-µCCP-OES and ICP-OES for metals from soil contaminated by the industry of non-ferrous metals [53].

Sample	Method	Ag	As	Cd	Cu	Pb	Sb	Sn	Zn
1	SSETV-µCCP-OES	17.2±0.6	90.4±4.4	21.0±3.6	1062±35	4560±164	108±10	23.2±1.8	428±16
	ICP-OES	16.9±0.8	90.9±0.6	23.1±1.6	1070±21	4475±90	100±10	23.3±0.4	424±12
2	SSETV-µCCP-OES	2.13±0.30	422±50	11.1±1.0	1498±26	1154±20	57.0±8.0	18.4±1.9	622±14
	ICP-OES	1.87±0.25	417±30	10.4±0.8	1488±35	1167±25	46.8±9.0	20.7±1.4	653±28
3	SSETV-µCCP-OES	5.53±0.26	149±6	10.8±0.5	573±18	2405±26	69.1±9.0	20.6±2.1	1447±151
	ICP-OES	5.48±0.20	147±8	9.9±0.6	566±17	2424±28	65.0±7.0	18.3±0.6	1480±120
4	SSETV-µCCP-OES	14.8±0.8	206±15	5.50±0.25	272±16	6447±100	113±15	21.3±3.1	942±20
	ICP-OES	14.2±0.6	192±12	5.30±0.40	260±20	6549±100	103±18	20.2±2.5	931±30

[a] U represents the extended uncertainty at 95% confidence level

Table 2.8. Results (mg kg^{-1}) of Hg determination from soil samples by SSETV-µCCP-OES and ICP-OES [53].

Sample	SSETV-µCCP-OES mean±U[a]	ICP-OES mean±U[a]
1	1.21±0.35	1.23±0.24
2	4.31±0.30	4.27±0.22
3	17.1±1.2	18.0±1.3
4	34.8±1.8	32.8±2.3

[a] U represents the extended uncertainty at 95% confidence level

2.6. Conclusions

It was demonstrated that the novel SSETV-μCCP-OES analytical system if useful for the determination of volatile elements with the excitation energy of the resonance lines up to 7 eV, with limits of detection in the order of ng ml^{-1} or pg. It was developed a method for Cd determination from foods based on the SSETV-μCCP-OES analytical system, with similar performance with the one of the standardized GFAAS method. The proposed method satisfies the requirements of the European legislation concerning the analytical performance of methods used in quality control laboratories. Also, a simultaneous multi-elemental method for determination of elements from soil samples was developed, which shows similar analytical performance with the one of the traditional ICP-OES method with pneumatic nebulization. Although the emission spectrum of elements is simple, fact that should be a disadvantage with regard to the analytical versatility, this fact is instead an advantage because consequently a low resolution microspectrometer could be used for the recording of the emission spectra. The novel analytical system and the developed methods are attractive and present the following advantages in comparison with the traditional ICP-OES method: (i) Simplicity of sample work-up and introduction in the microplasma; (ii) Similar or better limits of detection than in case of pneumatic nebulization; (iii) In comparison with ICP-OES, lower costs of the development and maintenance of the instrumentation, as a result of the low operating power and the reduced Ar consumption. The conducted research offered the possibility of widening the area of applicability of the microplasma sources and the corresponding instrumentation for elemental determinations from liquid microsamples, including the priority hazardous elements (Cd, Hg, Pb) from foods with complex matrices and environmental sample. However, it was observed that the SSETV-μCCP-OES analytical methods are affected by non-spectral matrix effects caused by Al, Fe, alkaline and alkaline earth elements, therefore the used of the standard addition method was necessary, instead of the external calibration. The avoidance of the non-spectral effects still represents a challenge for the microplasma sources and further research is required by the use of separation and preconcentration methods based on liquid-liquid microextraction and diffusion gradient thin film method.

CHAPTER III. MERCURY DETERMINATION METHOD FROM FOOD SAMPLES BASED ON COLD VAPOUR GENERATION AND DETECTION BY CAPACITIVELY COUPLED PLASMA MICROTORCH OPTICAL EMISSION SPECTROMETRY: ANALYTICAL CHARACTERIZATION AND COMPARISON WITH TD-AAS AND THE REQUIREMENTS OF THE EUROPEAN LEGISLATION

3.1. Situation at international level. Working hypothesis and objectives

Mercury, together with Cd and Pb, is a priority hazardous element in all of its forms, being extremely toxic, therefore it should be monitorized in extremely low concentrations in environmental, biological and food samples. Thus, mercury monitoring continues to be a research area of interest and forms the subject of several studies regarding exposure risk, development of sample work-up methods and development of analytical instrumentation [56,69-79]. Hg determination is a challenge for laboratories, and the requirements imposed for quality control labratories regarding the performance of the analytcal methods are regulated at Europen level [58-60]. The spectral methods used in laboratories for Hg determination from fish and foods are CV-AAS [80-89], CV-AFS [80-89], CV-ICP-OES [90,91], CV-ICP-MS [92-94], TD-AAS [95-102], HPLC-ICP-MS and GC-ICP-MS [103,104].

During the past ten years, besides the clasical laboratory instrumentation, the technology of microplasma was investigated for the development of a cheap but robust and sensitive analytical method used for Hg determination based on cold vapour derivatization [105-109].

In line with the worldwide interest, a high sensitivity analytical method, used for mercury determination for a large variety of foods, was investigated and characterized, which is based on cold vapour generation using a 20% solution of $SnCl_2$, stabilized in 15% HCl and detection with a fully miniaturized analytical system formed by a capacitively coupled plasma microtorch with low operating power and reduced Ar consumption (10 – 20 W, 150 – 200 ml min^{-1}) and a low resolution microspectrometer (0.4 nm FWHM). The novelty was represented by the interfacing of the *on-line* preconcentration of mercury vapours on a microcollector with gold filament with the plasma microtorch, which contributed to a remarcable improvement of the sensitivity of the method, as it exceeded the traditional analytical systems based on emission, absorption and atomic fluorescence. Furthermore, the comparison with the traditional TD-AAS and CV-AFS methods was envisaged, as well as the comparison with the requirements imposed by the European Committee in case of mercury determination from

foods. The CV-µCCP-OES method was applied not only in case of marine foods but also for foods from terrestrial vegetable and animal sources.

3.2. Fully miniaturized CV-µCCP-OES instrumentation

The experimental determinations were conducted on a CV-µCCP-OES prototype model with and without preconcentration of mercury vapour (OSIM patent granted), shown in Fig. 3.1 [110,111].

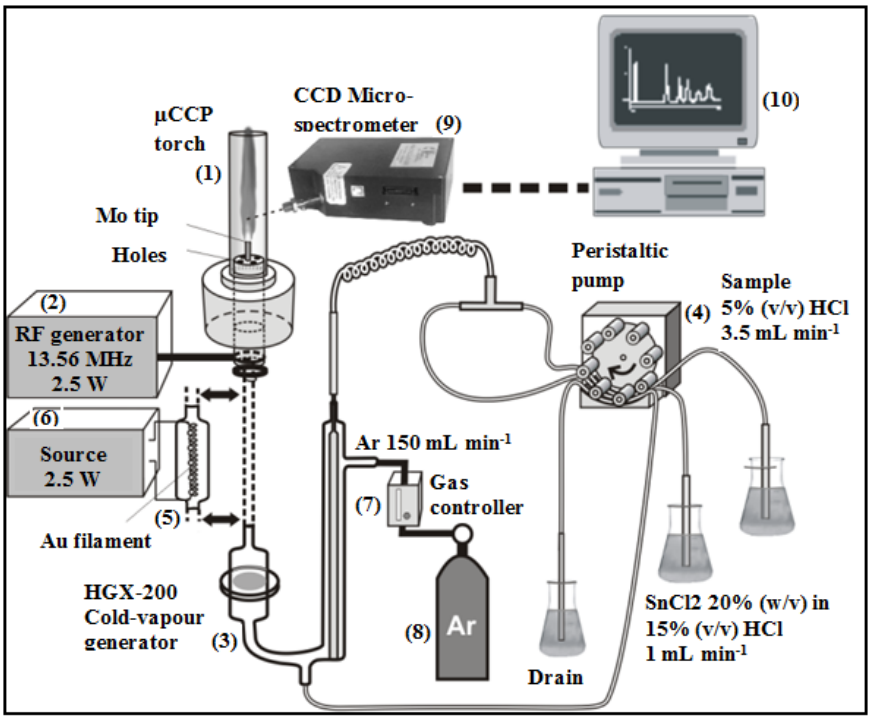

Fig. 3.1. Schematic diagram of the miniaturized CV-µCCP-OES anaytical system with and without gold microcollector [54,111].

The CV-µCCP-OES method is based on the cold vapour conversion of Hg^{2+} to Hg^0 by mixing the sample in HCl medium in continuous flow with a solution of $SnCl_2$ in HCl medium in a cold vapour generator. The mercury vapour are purged from the liquid phase with the Ar flow in the microplasma where their excitation takes place and the emission signal is measured at 253.652 nm wavelength with a microspectrometer. According to the Hg concentration in samples, the CV-µCCP-OES system was operated in two ways: *1. Without preconcentration of mercury vapour* [54] for the analysis of fish samples; *2. On-line preconcentration of mercury vapour* [111] for the analysis of food samples with very low Hg concentrations. The operating conditions are presented in Table 3.1 [105,108]. In case of the procedure without preconcentration the sample flow was mixed with the derivatization

reagent, while in case of the procedure with preconcentration the Hg vapour were preconcentrated from sample volumes of 25 ml, followed by thermal desorption by heating the Au filament and introduction of vapour in the plasma by an Ar flow. Twenty episode spectra of Hg emission were recorded at 253.652 nm. Background correction was carried out for each episode based on a post-desorption spectrum, while the net signal was obtained by summation of corrected episode emmisions.

Table 3.1. Operating conditions for mercury determination from foods by CV-μCCP-OES method.

Stage/parameters	Procedure without preconcentration. Fish samples [236]	Procedure with preconcentration. Other foods [291]
Chemical vapour generation		
HCl concentration in sample	5% (v/v) HCl	5% (v/v) HCl
Concentration of derivatization agent	20% (m/v) SnCl2 in 15% (v/v) HCl	20% (m/v) SnCl2 in 15% (v/v) HCl
Sample flow by HGX-200 generator	3.5 ml min^{-1}	3.5 ml min^{-1}
Derivatization agent flow	1 ml min^{-1}	1 ml min^{-1}
Washing time between samples	40 s with 5% (v/v) HCl	40 s with 5% (v/v) HCl
Plasma microtorch and Hg signal measurement		
Plasma operating power	10 W	20 W
Arfon flow	150 ml min^{-1}	200 ml min^{-1}
Plasma observation height	1.8 mm	1 mm
Wavelength	253.652 nm	253.652 nm
Signal integration time	8 s	8 s (episode signals)
Signal measurement	Peak height	Transient peak height from first episode
Base correction	Two point linear model	Two point linear model based on the baseline signal from a mercury post-desorption episode
Calibration	External 0 – 6 μg l^{-1} Hg (n=8)	External 0 – 10 ng l^{-1} Hg (n=12)
Preconcentration sample volume	-	25 ml
Gold filament heating	-	Voltage: 5 V; Electric power intensity: 1.5 A; Heating time: 5 s

3.3. Sample description and preparation

A total of ten samples of different types of fish and seventy vegetable and meat samples were analyzed, which were liophilized and mineralized in nitric acid and hydrogen peroxide in a microwave digestor, brought after in a medium of 5% (v/v) HCl and determined by CV-μCCP-OES and CV-AFS. TD-AAS determinations were conducted just in case of fish, directly in solid state [54,111].

3.4. CV-μCCP-OES method validation for the determination of Hg in food samples

For the validation of the CV-μCCP-OES method, a comparison with the TD-AAS method was carried out, for the determination of Hg directly from solids [112]. The applicability of the CV-μCCP-OES method in case of Hg determination was verified on fish muscles, foods from animal origin, vegetables and fruits, according to the 2002/657/EC, 2007/333/EC and 2011/836/EU decisions of the European Committee [58-60]. The analytical parameters considered for validation were: LOD, LOQ, precision and accuracy.

The characteristics of the calibration curves, LOD and LOQ of the CV-μCCP-OES system with or without Hg preconcentration in comparison with the TD-AAS method are presented in Table 3.2. According to the data of Table 3.2, the LOD and LOQ values of the proposed CV-μCCP-OES method for the analysis of fish meat are 160, respectively 55 times lower than admitted maximum concentration (500 μg kg^{-1}) and the method satisfies the requirements of the Decision 2007/333/EC [59]. The CV-μCCP-OES method shows better values of LOD and LOQ in comparison with the TDAAS method, calculated for 50 mg analyzed solid sample [54]. By applying the Hg preconcentration on the microcollector with Au filament, substantial improvement of LOD and LOQ can be obtained in case of CV-μCCP-OES method. In these conditions, the CV-μCCP-OES method can be applied for Hg determination from vegetables, fruits, different types of meat, rice and bread. The limit of detection of CV-μCCP-OES method with preconcentration is better than the ones reported in literature for the traditional methods used in case of Hg determination from biological and food samples, with or without preconcentration [81,83,92,95,96,113].

The results obtained by CV-μCCP-OES for Hg determination from fish CRM samples without preconcentration in comparison with TD-AAS and the ones obtained by CV-μCCP-OES with preconcentration from CRM samples of brown bread, chicken meat, apples, cabbage and carrots, are presented in Table 3.3 [54,111]. According to the data presented in Table 3.3, the CV-μCCP-OES method satisfies the requirement regarding the accuracy of Hg

determination from foods because the differences between the found values and the certified values are lower than ±10%, as indicated in Decision 2002/567/EC [58].

3.5. Real sample analysis for Hg determination from foods. Repeatability of the CV-μCCP-OES method

The results obtained in case of mercury determination from foods, which implied the preconcentration, are presented in Table 3.4. Furthermore, the results obtained by CV-μCCP-OES without preconcentration from ten test samples of fish muscle in comparison with TD-AAS are presented in Table 3.5 [54,111].

According to the data presented in Table 3.5, the precision of Hg determination from fish muscle by CV-μCCP-OES without preconcentration was in the 1.8% – 5.5% interval, similarly as in case of TD-AAS method (4.0 – 10.0%) [54]. If preconcentration was needed, the precision of the CV-μCCP-OES method for mercury determination from foods was 0.7 – 9.0%, for concentrations of 0.57 – 25.2 μg kg^{-1} Hg. The precision of the method satisfies the requirement for concentrations lower than 25 μg kg^{-1} Hg, where RSD should be lower than 20%, according to Decision 2002/657/EC [58].

Table 3.2. Characteristics of calibration curves, limits of detection and limits of quantification of Hg by CV-μCCP-OES with and without mercury vapour preconcentration in comparison with TD-AAS method conducted directly on solid state samples [54,111].

Method	Procedure	Calibration domain	Calibration sensitivity	Linear correlation coefficient (r)	LOD		LOQ		Reference
		($ng\ l^{-1}$)	(Peak height signal/$ng\ l^{-1}$)		($ng\ l^{-1}$)	($\mu g\ kg^{-1}$)	($ng\ l^{-1}$)	($\mu g\ kg^{-1}$)	
CV-μCCP-OES	Without preconcentration	0 – 6000	3.690±0.034	0.9999	12	3	36	8	[236]
CV-μCCP-OES	With preconcentration	0 – 10	1432±18	0.9998	0.02	0.005	0.06	0.015	[291]
TD-AAS	Directly from solid state	0 – 25	$1.21x10^{7}$±211097	0.9997	-	10	-	30	[291]

Table 3.3. Results obtained in case of Hg determination from food certified standard materials by CV-μCCP-OES with and without *on-line* preconcentration of mercury vapours by amalgamation on gold filament in comparison with the TD-AAS method directly from solids [54,111].

Reference material	U.M.	Certified value±U[a]	Found value±U[a] (n=5)		CV-μCCP-OES procedure	Reference
			CV-μCCP-OES	TDAAS		
BCR-463 Tuna Fish	$mg\ kg^{-1}$	2.85±0.16	2.83±0.11	2.78±0.06	Without preconcentration	[236]
DOLT-4 Dogfish liver	$mg\ kg^{-1}$	2.58±0.22	2.58±0.04	2.63±0.09	Without preconcentration	[236]
TORT-2 Lobster Hepatopancreas	$mg\ kg^{-1}$	0.27±0.06	0.29±0.02	0.28±0.02	Without preconcentration	[236]
BCR-191 Brown Bread	$\mu g\ kg^{-1}$	2.00[b]	1.95±0.08	-	With preconcentration[b]	[291]
GBW-10018 Chicken	$\mu g\ kg^{-1}$	3.6±1.5	3.6±0.2	-	With preconcentration[b]	[291]
GBW-10019 Apple	$\mu g\ kg^{-1}$	2.00[b]	1.90±0.02	-	With preconcentration[b]	[291]
IAEA-359 Cabbage	$\mu g\ kg^{-1}$	13±2	12±1	-	With preconcentration[b]	[291]
IC-CS-CR-2 Carrot Root	$\mu g\ kg^{-1}$	4.3[b]	4.2±0.2	-	With preconcentration[b]	[291]

[a] U represents the extended uncertainty at 95% confidence level; [b] Preconcentration of Hg vapours from 25 ml sample on gold filament

Table 3.4. Results obtained for Hg determination from foods by CV-μCCP-OES with *on-line* preconcentration by amalgamation on gold filament [111].

Sample	Number of samples	U.M.	Content					U_f [b]
			Min	Max	Mean	s_r [a]	RSD (%)[a]	
Chicken meat	6	μg kg^{-1}	2.34	4.42	3.36	0.04-0.08	0.9-3.6	0.47
Carrot, celery, parsnip, parsley	8	μg kg^{-1}	11.0	20.4	15.6	0.2-0.5	0.9-2.9	2.2
Tomato, pepper, cucumber	11	μg kg^{-1}	1.87	3.35	2.4	0.03-0.11	1.3-4.4	0.37
Onion	5	μg kg^{-1}	12.5	15.9	14.3	0.2-0.3	1.3-2.5	2.5
Cabbage	8	μg kg^{-1}	2.23	9.11	5.0	0.06-0.28	0.7-5.3	0.44
Potato	5	μg kg^{-1}	10.6	11.7	11.2	0.2-0.3	1.8-2.6	2.2
White and black grape	5	μg kg^{-1}	3.18	4.23	3.57	0.05-0.07	0.9-1.9	0.15
Apple, pear, peach, nectarine	12	μg kg^{-1}	1.25	2.53	1.76	0.03-0.09	1.7-6.0	0.25
White and black bread	5	μg kg^{-1}	0.57	1.84	1.25	0.04-0.08	3.8-9.0	0.11
Rice	5	μg kg^{-1}	20.0	25.2	22.8	0.2-0.6	0.9-2.2	4.1
Green salad	5	μg kg^{-1}	0.75	2.60	1.70	0.05-0.07	2.0-7.7	0.15

[a] – s_r and RSD – standard deviation and relative standard deviation of repeatability (n=5 complete mineralizations/analysis sequences for each sample)

[b] – maximum value of standard uncertainty calculated for the lowest concentration in the domain of interest

Table 3.5. Results (mg kg^{-1}) of Hg determination in test samples of fish tissue by CV-μCCP-OES without preconcentration and TD-AAS directly for solids [54].

Sample	CV-μCCP-OES		TD-AAS	
	Mean±U[a]	RSD (%)[b]	Mean±U[a]	RSD (%)[b]
1	0.18±0.01	4.6	0.17±0.02	10.0
2	0.25±0.02	5.5	0.24±0.01	9.4
3	0.38±0.02	4.2	0.36±0.02	5.0
4	0.53±0.02	3.4	0.55±0.03	4.5
5	0.28±0.02	4.7	0.26±0.02	5.9
6	0.24±0.01	4.7	0.22±0.02	8.8
7	0.28±0.01	3.2	0.29±0.02	4.8
8	0.32±0.02	5.4	0.34±0.02	5.0
9	0.62±0.02	2.7	0.65±0.03	4.0
10	0.76±0.02	1.8	0.74±0.04	4.1

[a] U represents the extended uncertainty at 95% confidence level

[b] RSD represents the percent relative standard deviation for five repeated measurements

3.6. Conclusions

It was demonstrated that analytical method based on clasical cold vapour derivatization with $SnCl_2$ developed in a cheap and fully miniaturized CV-μCCP-OES laboratory system, with or without *on-line* preconcentration of Hg vapours on a gold filament, can be successfully used for mercury determination in case of a large variety of foods, even at extremely low concentrations.The introduction of the preconcentration stage permitted a remarcable improvement of the limit of detection values in comparison with the traditional methods based on atomic emission, absorption and atomic fluorescence. The interfacing of the miniaturized device for *on-line* preconcentration of mercury vapour with the plasma microtorch is beneficial and can be easily used. The CV-μCCP-OES method satisfies the requirements imposed by the European Committee for the analytical methods for Hg control in foods.

CHAPTER IV. MERCURY DETERMINATION METHOD BASED ON SONO-INDUCED COLD VAPOUR GENERATION AND DETECTION BY CAPACITIVELY COUPLED PLASMA MICROTORCH OPTICAL EMISSION SPECTROMETRY: ANALYTICAL CHARACTERIZATION AND COMPARISON WITH ATOMIC FLUORESCENCE SPECTROMETRY

4.1. Situation at international level. Working hypothesis and objectives

The miniaturization of instrumentation and development of environment and human friendly analytical methods which satisfy the requirements regarding analytical performance of some analyses and also the requirements of GAC, represent emergent fields in the atomic spectrometry [4]. One of the research directions in the field of GAC concerning elemental analyses, which involves an intermediary stage of derivatization, is the foto-induced chemical vapour generation under the influence of UV radiations (UV-PVG) [114-123], as well as the sono-induced could vapour generation (SICV) [124,125], as alternative methods for the conventional chemical derivatization with sodium borohydride or stannous chloride in hydrochloric acid medium. These unconventional methods present major advantages, specifically: 1. Low cost by the elimination of expensive chemical reagents; 2. Use of biodegradable organic acids; 3. Decrease of non-spectral interferences; 4. Easy optimiziation of analytical systems by decresing the number of variables which have influence on the derivatization process [69,70,73,74,126,127].

The aim of this study was, worldwide for the first time, the investigation of the capability and analytical applicability of sono-induced cold vapour generation, interfaced with optical emission spectrometry in a capacitively coupled plasma microtorch with low operating power and reduced argon consumption and a microspectrometer (SICV-μCCP-OES) for mercury determination, as alternative for the clasical derivatization with $SnCl_2$ or $NaBH_4$, discussed in the previous study (Chapter III). The SICV-μCCP-OES method is based on mercury vapour generation in formic acid medium in a batch sonoreactor, *on-line* preconcentration of mercury vapour by amalgamation on a microcollector with gold filament, introduction of mercury vapour, after desorption from the filament, in a plasma with low opering power and reduced Ar comsumption and mercury episode emission spectra measurement with a low resolution microspectrometer. The method was used for soil and marine food samples and was compared with the traditional methods, such as CV-AFS. After optimization of the method, the analytical performance and the non-spectral interferences of the mineral and organic matrix were investigated.

4.2. SICV-µCCP-OES instrumentation and working procedure

The experimental SICV-µCCP-OES equipment is depicted in Fig 4.1 [128].

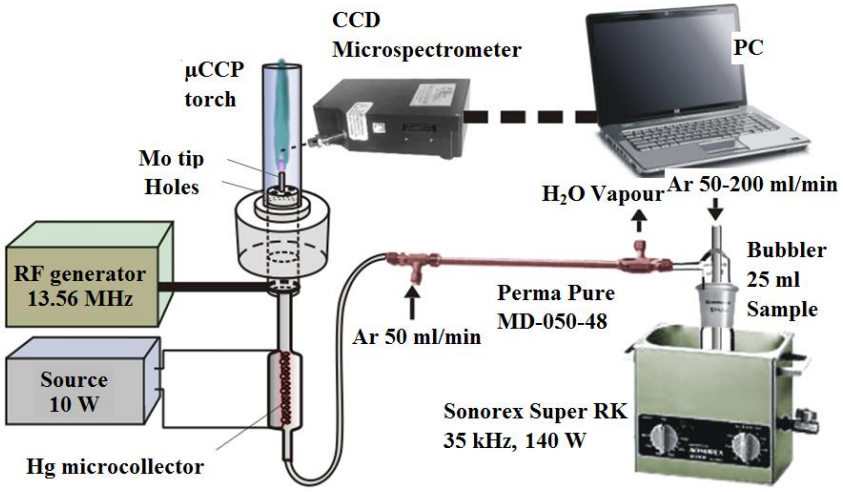

Fig. 4.1. Schematic diagram of the experimental SICV-µCCP-OES system with microcollector with gold filament [128].

The operating procedure of the SICV-µCCP-OES system was the following [128]: a volum of 25 ml aqueous solution of formic acid 0.2 mol l^{-1} was added in the sonoreactor. Aliquot volume of 2 – 500 µl of 100 ng ml^{-1} Hg stock solution, solution of CRM samples or test samples was added. The purging of the argon flow was adjusted to 50 – 200 ml min^{-1}. The sample was sonicated for 10 min at 140 W. The generated mercury vapour were purged by the Ar flow from the sonoreactor and captured on the gold filament of the microcollector at room temperature. After the trapping stage, the plasma was started and the mercury vapour were desorbed from the filament by heating for 5 s at voltage of 5 V applied from the HM 7042-5 source and an electrical power of 1.5 A. The mercury vapour were introduced in the plasma by an argon flow of 50 – 200 ml min^{-1}. The argon contraflow for the removal of water vapour from the Nafion tube was maintained at a constant value of 50 ml min^{-1}. Twenty episode spectra were registered simultaneously with the desorbtion of mercury vapour, with integration time of 500 ms per episod. Only the first five episode spectra were selected which contained the Hg episode signals. The net emission signal of mercury for each episode was obtained after baseline correction on both sides of the spectral line, by using the linear model of interpolation of the spectral background at Hg line of 253.652 nm. The total net signal of Hg was obtained by summation of the episode net signals.

4.3. Sample description and preparation procedure

Quantities of 500 mg CRM samples, fish tissue or organs were mineralized with 8 ml nitric acid and 4 ml hydrogen peroxide in the microwave digestor. In case of soil samples, quantities of 200 mg were dissolved in mixture of 10 ml HNO_3, 2 ml H_2O_2 and 4 ml HF. The Hg content of the filtrates was determined by SICV-µCCP-OES and CV-AFS, the metal content by ICP-OES, the anion (Cl^-, F^-, NO_3^-, SO_4^{2-} and PO_3^{3-}) content by ion chromatograpy, as well as the content of residual organic matter was determined after mineralization [128].

4.4. Optimization of working parameters of the SICV-µCCP-OES system

In order to obtain better analytical performance, the parameters which have influence on the generation of mercury vapour were optimized, such as concentration of formic acid as derivatization agent, sonication time, the argon flow used for mercury vapour stripping from the sonoreactor, as well as the working parameters of the plasma microtorch, such as the argon flow used for the plasma sustaining, the operating power and spectroscopic observation height. All optimized conditions of the SICV-µCCP-OES system are presented in Table 4.1 [128].

Table 4.1. Working conditions for mercury determination by SICV-µCCP-OES [128].

Stage/parameters	Setting
Chemical vapour generation (sonicated sample)	
Electric power/frequency	140 W/35 kHz
Formic acid concentration in sample	0.2 mol l^{-1}
Sonication time	8 min
Mercury vapour preconcentration on gold filament	
Voltage on filament in desorbtion stage	5 V
Electric power intensity in filament in desorbtion stage	1.5 A
Filament heating time	5 s
Plasma microtorch and Hg signal measurement	
Electric power of plasma	10 W
Argon flow	100 ml min^{-1}
Plasma observation height	0.8 mm
Wavelength	253.652 nm
Hg emission signal measurement	20 episode spectra recorded, 500 ms integration time/episode and summation of episode net signals
Calibration	External in 8 points 0 – 0.2 ng ml^{-1}; Sample volume 25 ml (0 – 5 ng Hg)

4.5. SICV-μCCP-OES method validation for the determination of Hg

For the validation of the SICV-μCCP-OES method, the performance and the obtained analytical results were compared with the traditional CV-AFS method which is currently used in laboratories for Hg determination. The determinations were conducted with the fully miniaturized Hydra-AF Mercury Analyzer (Teledyne Leeman Instruments, USA) [54,129]. The SICV-μCCP-OES method was validated regarding the non-spectral effects of the multimineral and organic matrix, LOD and LOQ in biological and environmental samples, precision and trueness by analysis of CRM samples, soil and fish muscle test samples, comparison with the traditional CV-AFS method with clasical derivatization with stanneous chloride in HCl medium and atomic sprectrometry methods based on microplasma sources. The preliminary measurements conducted by SICV-μCCP-OES indicated a depressive effect up to 60% in presence of 5% (v/v) HCl for the generation of cold vapour in 0.2 mol l^{-1} formic acid medium, in comparison with the solution without HCl. In order to eliminate this influence, the samples were diluted at an appropriate level before analysis. Therefore, the depressive effects of the metal, anion and residual organic matter were negligible. The viability of the method was verified by the Hg recovery obtained in case of CRM samples. The results indicated that there were no systematic errors for a soil aliquote sample of 200 mg, mineralized at 50 ml, or 500 mg of fish tissue/organs at 25 ml, followed by a dilution in the interval of 50 – 12500 times, and a concentration (μg l^{-1}) up to 20 (Cu), 85 (Pb), 40 (Zn), 5800 (Fe), 150 (Mn), 16 (Co), 7 (Ni), 3 (Ag), 30 (Cd), 30 (As), 30 (Cr) and anions (mg l^{-1}) 2 (Cl^-), 2.5 (SO_4^{2-}), 2160 (NO_3^-), 525 (F^-), 0.3 (PO_4^{3-}) and 40 mg l^{-1} TOC. The parameters of the calibration curve and LODs obtained in three succesive days are presented in Table 4.2 [128].

Table 4.2. Parameters of calibration curve and limits of detection of mercury for the SICV-μCCP-OES method in three successive days [128].

Day	Calibration domain (ng)[a]	Y-intercept	Slope (peak signal height ng^{-1})	r	$s_{y/x}$[b]	LOD ($ng\ l^{-1}$)	LOD (pg)
1	0 – 5	139.9	2025.5	0.9995	128.2	4.8	121
2	0 – 5	14.3	2045.2	0.9997	96.6	5.4	154
3	0 – 5	42.2	1949.7	0.9997	94.0	4.9	123
Mean	0 – 5	65.6±66.0	2006.8±50.4	0.9996± 0.0001	106.3± 19.0	5.0±0.3	125±8

[a] n=6 points of calibration; 0 – 0.2 ng ml^{-1} Hg in 25 ml sample;

[b] Standard deviation of residuals calculated from the equation of the calibration curve [112]

The limit of detection of 5.0±0.3 ng l^{-1} Hg and the absolute one of 125±8 pg Hg allows the determination of Hg by SICV-μCCP-OES method from liquid samples with concentrations starting at 15 ng l^{-1}. Mercury can be determined from soil by SICV-μCCP-OES method at aconcentrations above 355 μg kg^{-1}. The value of the LOD in biological (fish) samples is 25 μg kg^{-1}. A comparison of LOD obtained by the SICV-μCCP-OES method with the LOD values obtained by other methods based on microplasma sources is presented in Table 4.3 [128].

Table 4.3. Comparison between mercury limit of detection obtained by SICV-μCCP-OES method and other analytical systems with microplasmas [128].

Method	LOD (ng l^{-1})	Derivatization system	Preconcentration	Reference
SICV-μCCP-OES	5±0.3	Sonication (0.2 mol l^{-1} HCOOH)	Yes	128
CV-μCCP-OES	0.02	$SnCl_2$ – HCl	Yes	107
CV-μCCP-OES	12	$SnCl_2$ – HCl	No	108
CV-Pdc-OES	0.08	$SnCl_2$ – HCl	Yes	106
CV-AFS	12	$SnCl_2$ – HCl	No	108
CVG-μAPGD-OES	140	$SnCl_2$ – HCl	No	130
CV-MSP-OES	640	$SnCl_2$ – HCl	No	33
CV-DBD-OES	2800	$SnCl_2$ – HCl	No	131

The results obtained in case of analysis of CRM samples of fish tissue, organs, soil and sediments, in comparison with CV-AFS are presented in Table 4.4 [128]. The data suggest good consistency between the results obtained by SICV-μCCP-OES and the certified ones, respectively the ones obtained by CV-AFS with chemical derivatization with $SnCl_2$ [128].

Table 4.4. Results obtained for mercury determination from CRM samples of fish muscle, organs, soil and sediments by SICV-μCCP-OES and CV-AFS [128].

Reference material	Certified value±U (mg kg^{-1})	Found value±U (mg kg^{-1})	
		SICV-μCCP-OES	CV-AFS
CRM048050G	28±1.13	28±0.97	28±0.87
RTC-CRM025-050	99.8±31.7	99.3±1.00	99.3±1.00
LGC6135	3.2±0.4	3.1±0.2	3.3±0.2
LGC6141	1.2	1.2±0.06	1.2±0.03
NCSDC78301	0.22±0.04	0.23±0.02	0.24±0.03
BCR280R	1.46±0.2	1.44±0.04	1.39±0.09
DOLT-4	2.58±0.22	2.53±0.07	2.59±0.09
TORT-2	0.27±0.06	0.26±0.01	0.28±0.02
BCR463	2.85±0.16	2.82±0.05	2.83±0.06

4.6. Real sample analysis for Hg determination by SICV-μCCP-OES

Table 4.5 presents the results gained after analysis of real samples of fish muscle and soil.

Table 4.5. Comparative results obtained for mercury determination from real samples of soil and fish by SICV-μCCP-OES and CV-AFS [128].

Sample	SICV-μCCP-OES Mean±U (mg kg^{-1})	CV-AFS Mean±U (mg kg^{-1})
Soil		
1.	0.06±0.002	0.06±0.002
2.	28.2±0.5	28.3±0.6
3.	45.6±1.7	44.5±1.5
4.	2.63±0.05	2.70±0.07
5.	1.08±0.07	1.15±0.06
6.	1.05±0.06	1.10±0.05
Fish		
1.	0.12±0.002	0.12±0.002
2.	0.14±0.009	0.15±0.01
3.	0.17±0.007	0.18±0.01
4.	0.21±0.01	0.22±0.01
5.	0.18±0.01	0.19±0.007
6.	0.11±0.01	0.10±0.009

4.7. Conclusions

It was demonstarted that the cold vapour generation by sonication in formic acid can be easily interfaced with a capacitively coupled plasma microtorch with low operating power and low argon consumption and detection by optical emission spectrometry by using a low resolution microspectrometer for mercury determination from different samples. The SICV-μCCP-OES method satisfies the majority of the requirements of the green analytical chemistry and presents a few practical advantages in comparison with the current conventional methods, by excluding expensive derivatization reagents and reaction medium (ultrapure $SnCl_2$, $NaBH_4$ and HCl) and using a cost-effective miniaturized intrumentation as microplasma source and spectral detector. The characteristics of SICV-μCCP-OES method are good sensitivity, reasonable precision and accuracy, therefore it can be successfully used for Hg determination from biological and environmental samples with complex matrices, as alternative for the conventional CV-AFS method which implies chemical vapour generation with $SnCl_2$ in HCl medium. The non-spectral effects caused by transition metals, anions and organic matter were eliminated by the simple dilution of the samples.

CHAPTER V. ARSENIC BEHAVIOR AND CHEMICAL MODELING OF GROUNDWATER FROM THE BANAT PLAIN, SOUTHWESTERN ROMANIA, BASED ON ARSENIC SPECIATION AND CO-OCCURING SPECIES IN THE GROUNDWATER, BY COMBINING UNSUPERVISED MULTIVARIATE STATISTICAL WITH DIAGRAMS

5.1. Situation at international level. Working hypothesis and objectives

Groundwater is one of the most important source of drinking water, human activities and leisure, irrigation and industry. Therefore, the quality evaluation of groundwater and health hazards of elemental contaminants were objectives of several studies [132-138]. One of the common contaminants of groundwater, the naturally occuring arsenic appears as inorganic species (arsenite and arsenate), as result of the water-rock interaction from aquifer rich in arsenic. In Europe, including Eastern Hungary, Western Romania, Northern Serbia, North-Eastern Croatia and Southern Slovakia, the Pannonian Basin is characterized by high natural content of As in the groundwater, representing health hazard for more than 1000000 inhabitants by drinking water consumption [139-142]. Examination of groundwater with high As concentration and its mechanism of occurance are of worldwide interest regarding public health and environment [143-151]. Arsenic is present in the environment in its forms of inorganic (arsenite-As(III), arsenate-As(V)) and organic (monomethylarsonic and dimethylarsinic acid) species with different toxicities. The inorganic species present higher toxicities, therefore the arsenites and arsonic acid are included in Group I human carcinogens [152,153]. World Health Organization (WHO) and U.S. Environmental Protection Agency (EPA), adopted the value of 10 $\mu g\ l^{-1}$ as MCL of As in drinking water [154,155]. Based on the Water Framework Directive (WFD 2000/60/EC), the European states adopted the Groundwater Directive (GWD 2006/118/EC) with the aim of protecting the surface and groundwaters against pollution, and established environmental quality measures and standards to ensure that the water resources could reach a „good stage" [156-159]. The member states of the EU established threshold values (TVs) for the groundwater bodies, according to the hydrogeological conditions and natural background levels (NBLs), at least for the pollutants declared as health hazards, with natural or anthropogenic occurance (As, Cd, Pb, Hg, NH_4^+, Cl^-, SO_4^{2-}, NO_3^-) and synthetic substances (trichloroethylene, tetrachloroethylene) [160]. The simple interpretation of the results of the study of hazardous substances in groundwater, in

comparison with the permitted values from guides, is not sufficient to explain and understand their behavior in the groundwater. Supervised/unsupervised multivariate statistical approaches are necessary in order to highlight the hidden connections between chemical parameters and establish relevant characteristics for the classification and delimitation of groundwater sources [133,134,136,140,161-164].

The aim of this study was the evaluation of As species behavior and chemical modeling of groundwater from the Banat Plain, in order to establish the occurance mechanism of As and other species like F^-, SO_4^{2-}, PO_4^{3-} şi NO_3^-, in high concentrations. The chemical modeling was based on the combination of water classification diagrams (Gibbs, Piper and Stuyfzand Hydrogeochemical Classification System (SHCS)) with unsupervized chemometric tools (cluster analysis – CA, principal component analysis – PCA, fuzzy principal component analysis – FPCA and fuzzy hierarchical cross-clustering – FHCC). The usefulness of the model was demonstrated on water samples collected from shallow (GW-ROBA03) and depth (GW-ROBA18) waterbodies.

5.2. Zone description, water sample collection and preservation

The chosen zone of study was the Banat Plain between the rivers Bega and Timiş, belonging to the Pannonian Basin, where very thick deposits of sediments were accumulated in the Neogene and Quaternary. The Quaternary deposits were completely covered by the ones of Pliocene, which were generally fine sediments, with thickness of 100 m in the east and 1000 m in the west. The groundwater bodies are overlapped in these deposits, a shallow (GW-ROBA03) between 15 m and 30 m, and a depth (GW-ROBA18) waterbody, down to 350 m [165].

Eighteen samples were collected, four from GW-ROBA03 and fourteen from GW-ROBA18. The water samples were filtered on-site through filters of 0.45 µm in polyethylene vials. The pH, E_h and alkalinity were measured and, after freezing, the samples were transported in the laboratory and stored at -20 ºC. As speciation, anion content, conductivity and TDS were measured on original samples without any treatment, whereas metals were determined after acidification with 2% (v/v) HNO_3. Ten samples of clay and sand were collected from the zone and investigated by X-ray diffraction (XRD), therefore the presence of quartz, sodium aluminosilicates, potassium, calcium and magnesium, carbonates, phosphates and fluorine was demonstarted [166].

5.3. Water sample preparation for arsenic determination and speciation by HG-µCCP-OES. Speciation procedure

In this study the determination and speciation of As(III) and As(V) was conducted by a non-chromatographic method based on selective derivatization of As(III) to arsine and detection by HG-µCCP-OES [167]. The scheme of the principle of the instrumentation is depicted in Fig. 5.1 [168].

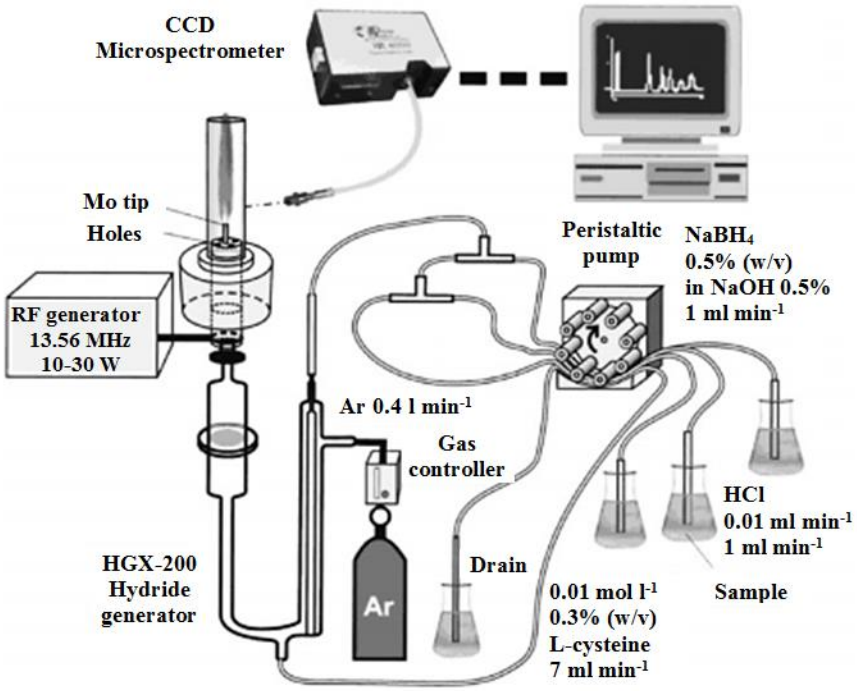

Fig. 5.1. Scheme of the principle of the HG-µCCP-OES equipment used for As determination and speciation in groundwater [168]

The working conditions for As(III) and As(V) speciacion and operation of the HG-µCCP-OES equipment are presented in Table 5.1 [166].

5.4. Quality assurance/Quality control for the analytical procedures

The results obtained in case of As determination by HG-µCCP-OES and metal detarmination by µCCP-OES from certified standard water samples indicated that the accuracy of As determination by HG-µCCP-OES was in the range of 100±9%, while the precision in the range of 1.2 – 1.7% in case of As(III), 3.1 – 9.5% for As(V) and 2.9 – 8.5 % in case of total As, for n=3 parallel measurements and 95% confidence level. The recovery of As species by selective derivatization was between 98 – 105% for As(III) and As(V) and 98 –

104% for total As [169]. The limit of detection of As was 0.2 μg l^{-1} [170]. The μCCP-OES method was validated for Na^+, K^+; Ca^{2+} and Mg^{2+} determination from water with 93 – 107% recovery and 2.0 – 3.9% precision.

Table 5.1. Stages and working conditions of As(III) and As(V) speciation from water samples by HG-μCCP-OES [166].

Stage/description	
As(III) determination	The pH of a 10 – 40 ml water sample was adjusted to 2.00±0.01 by potentiometric titration, 5 ml solution of 3% L-cysteine in 0.01 mol l^{-1} HCl was added. The obtained solution was diluted to 50 ml with HCl solution (pH 2.00±0.01) and the arsine was immediately generated.
Total As determination Sum of As(III) and As(V)	5 ml solution of 3% L-cysteine in 0.01 mol l^{-1} HCl was added to 10 – 40 ml of water and the prereduction of As(V) took place by heating in water bath for 10 min at 90±5 ºC. The pH was adjusted at 2.00±0.01 by potentiometric titration, the obtained solution was diluted to 50 ml with HCl (pH 2.00±0.01) and the arsine was generated.
As(V) determination	By difference of total As and As(III)
Conditions of arsine generation by As(III)	
Hydrid generator coupled with microtorch	HGX-200 CETAC, Nebraska, USA
Final L-cysteine concentration in sample	0.3%
HCl concentration/final pH of sample	0.01 mol l^{-1}/pH 2.00±0.01 adjusted before derivatization
HCl concentration/pH of carrier fluid	0.01 mol l^{-1} HCl/pH 2.00±0.01
Concentration of derivatization reagents	0.5% soultion of $NaBH_4$ stabilized with 0.5% NaOH
Sample flow	7 ml min^{-1}
Carrier fluid flow	1 ml min^{-1}
Derivatization reagent flow	1 ml min^{-1}
Plasma operating conditions and recording of spectra	
Optical detection	QE65 Pro microspectrometer, Ocean Optics, Dunedin, USA
Data acquisiotion and signal processing	Baseline correction with solution of 3% L-cysteine in 0.01 mol l^{-1} HCl (pH 2.00±0.01) as blank, signal integration time 5 s
Plasma operating power	10 W
Argon flow	150 ml min^{-1}
Plasma viewing	Radial, direct signal colection with lens with 10 mm focal length
As wavelength	228.812 nm, peak height measurement
Calibration range	0 – 100 ng ml^{-1} As

5.5. Multivariate statistical methods used for groundwater characterization

CA, PCA, FPCA and FHCC algorithms were used for chemical modeling of groundwater and arsenic's and other contaminants' behavior in aquifer [171-173].

5.6. Hydrogeochemical characteristics and summary statistics

Both GW-ROBA03 and GW-ROBA18 bodies are characterized by high As and phosphate concentrations. Therefore, the total As concentration was in the range of 3.6 – 77.3 μg l^{-1}, with a median of 24.0 μg l^{-1}, with exceeding of the TVs/CMA value in proportion of 72% of the number of analyzed samples. The more toxic As(III) species were in the range of 0.5 – 18.8 μg l^{-1}, with a median of 12.9 μg l^{-1} and exceeding of TVs/CMA in 50% of samples. The concentration of As(V) species was in the interval of 2.9 – 63.2 μg l^{-1}, with a median of 9.8 μg l^{-1} and exceedance of TVs/CMA in half of the samples. Regarding distribution, the majority species was As(V) with a percentage in the interval 57±20% in water samples with total As content above TVs/CMA (10 μg l^{-1}) and 73±18% in samples with As content below TVs/CMA. The percentage of As (V) species was 69±11% in samples with total As content above median. The phosphate concetration in water samples from the shallow GW-ROBA03 body was between 3.02 – 5.91 mg l^{-1}, exceeding the TV of 1.5 mg l^{-1}. In case of water samples from the depth GW-ROBA18 body the phosphate concentration was between 0.05 – 6.03 mg l^{-1}, exceeding TVs of 1.5 mg l^{-1} in twelve points from the fourteen analyzed ones. The phosphate TVs are consistent with the mineralogical composition of aquifer, where traces of Na, K and Ca phosphates were identified by XRD. Regarding nitrate concentration, the CMA value of 50 mg l^{-1} was exceeded only in one sample collected from 4 m depth, in which the content was 151 mg l^{-1}. This emphasises an anthropogenic contamination by the use of chemical or natural fertilizers in agriculture. The same sample was characterized by high sulfate concentration, 87.4 mg l^{-1}, however lower than TVs of 250 mg l^{-1}. The pH of groundwaters was in a weakly basic domain (8.13 – 8.49) with a median of 8.41, and it was fitted in the domain of normal values of drinking water, according to Law 458/2002 from Romania [174]. The basic pH is caused by the presence of Na^+ and HCO_3^- ions, as they represent the majority of ions in water, and clay soil, respectively.

According to the River Basin`s Management Plan of the Banat River Basin Administration, the shallow GW-ROBA03 body is in poor condition because of nitrate, while the depth GW-ROBA18 body is in good condition, meaning that the found high values of As and phosphate reflect just a local case and not the entire waterbody [165].

5.7. Nature of groundwater determined by diagrams

The Gibbs diagram [175] for cations (TDS *versus* $Na^+/Na^+ + Ca^{2+}$) and anions (TDS *versus* $Cl^-/Cl^- + HCO_3^-$) (mg l^{-1}) highlighted the fact that all water samples fall within the region dominated by rocks, where the geochemical composition of aquifer exhibits a powerful influence on the hydrogeochemical characteristics and type of groundwater. The leaching carried out on sand and clay samples indicated the fact that the main process which contributes to the occurance of As, PO_4^{3-} and HCO_3^- species and the weakly alkaline pH in the studied waterbodies is represented by the water-rock interaction, specifically the hydrolysis of silicates and phosphates, dissolution of Ca and Mg carbonates by rainwater with pH=5.6 and CO_2 content, respectively the desorbtion-adsorption processes from/on clays. The Piper diagram [176,177] revealed that 13 samples of the 18 analyzed ones are included in the Na^+ - HCO_3^- type of water, typical for the oxidant aquifer formed by fine sediments, four samples are of type Na^+ - Ca^{2+} - HCO_3^- and one single sample belong to the type Mg^{2+} - HCO_3^-[166].

5.8. Chemometric modeling of groundwater from the Banat Plain

The dendrogram presented in Fig. 5.2 divides the chemical parameters of groundwater into two clusters, C1 and C2.

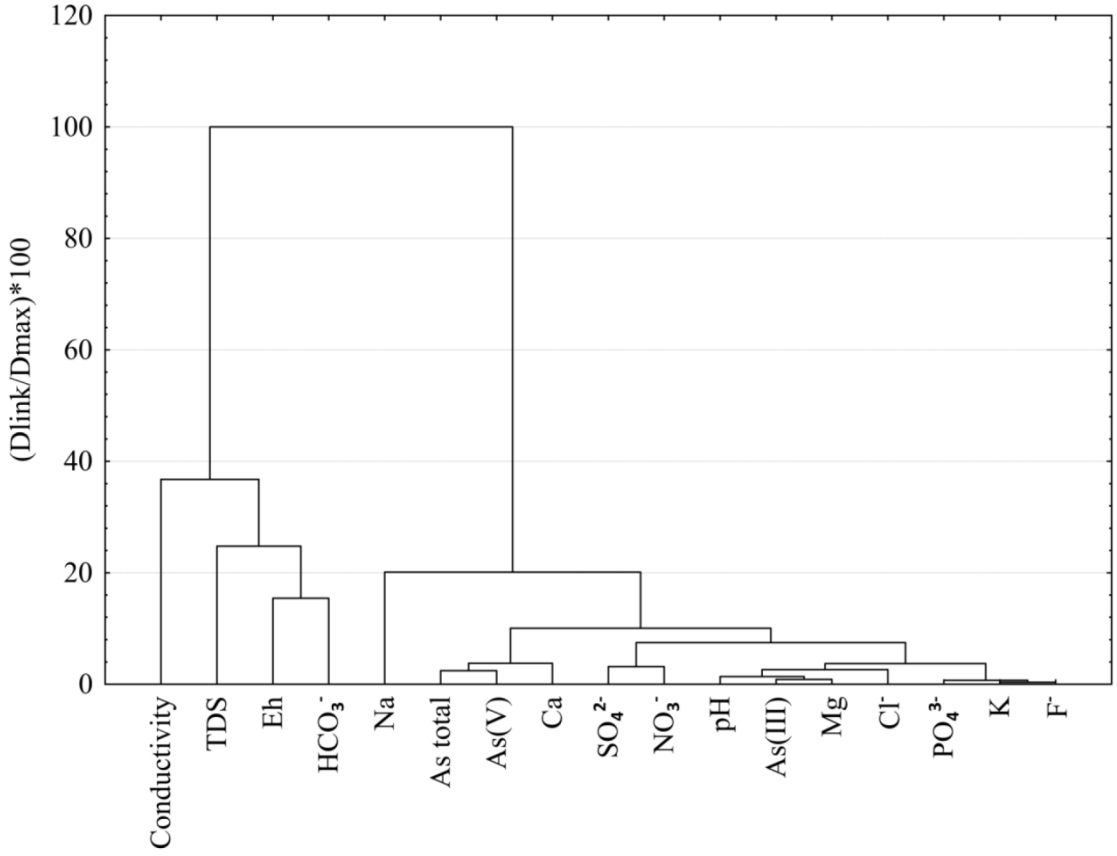

Fig. 5.2. Clustering of characteristics of groundwater from the Banat Plain [166].

The first cluster was assigned to the general characteristics of groundwater (EC, TDS, E_h şi HCO_3^-), which describe the salinity, alkalinity and redox state. The second cluster is more complex and shows the connections between cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (SO_4^{2-}, NO_3^-, PO_4^{3-}, F^-, Cl^-) which could be associated with the groundwater-rock long time interaction or field activities which affect the quality of water. The presence of As species in this cluster leads to the conclusion that As originates from natural sources such arsenic-binding Ca^{2+} and Mg^{2+} rocks because an association between Ca^{2+}, Mg^{2+}, pH, As(III), As(V) and total As could be observed [166]. Cluster analysis applied on water samples resulted with the identification of two groups (C1, nine samples) and (C2, eight samples), based on the similar characteristics related to lithology, while sample 1 is a singular one. The C1 cluster contains samples with low concentrations of individual As species and total As, cations and anions, low EC and TDS values, while C2 cluster consists of samples with As concentration >50 μg l^{-1} and higher values for other chemical parameters. Sample 1 with high As content does not fit within either cluster and can distinguished by the highest content of NO_3^-, SO_4^{2-}, TDS, high conductivity, high PO_4^{3-} content and lowest alkalinity, in comparison with the other samples.

The influencing factors after the normalized Varimax rotation show that the first five major components describe 90.2% of the total variation.

The first factor (F1) describes 29.9% of the variation and it was associated with the field activities, like the use of NPK fertilizers with high impact on shallow groundwater. The weak correlations of As species with the anthropogenic characteristics indicate the fact that there is no anthropogenic source of As from human activities and the high concentrations of As species in the groundwater of the Banat Plain are determined by the adsorbtion-desorbtion processes on/from clays and silicate hydrolysis in aquifer. These findings are consistent with the connections found in the next factors. F2, F3 and F4 factors present 17.9%, 15.1% and 19.8% and describe the natural enrichment of groundwater from the aquifer of Banat Plain with As species, under the influence of HCO_3^-, PO_4^{3-} and oxidative conditions. The positive correlations between As, HCO_3^- and PO_4^{3-} species indicate the increase of As mobility from aquifer into groundwater, under the influence of these anions. The F3 and F5 components explain the occurance of F^- anion in the groundwater, under the action of HCO_3^- and alkaline pH, but in a different pathway, compared with As occurance. The process was associated with the dissolution of CaF_2 under the action of HCO_3^-, $CaCO_3$ precipitation and Na^+ - Ca^{2+} ionic exchange, in order to compensate the negative charge excess [178,179].

Table 5.2. Influencing factors after Varimax rotation, which describe the variability of the chemical composition of groundwater from the Banat Plain [166].

	F1	F2	F3	F4	F5
F^-	0.020	0.056	0.334	0.103	**-0.852**
Cl^-	0.229	0.069	0.422	0.595	0.507
NO_3^-	**0.961**	-0.070	-0.127	-0.073	0.032
PO_4^{3-}	0.479	0.547	-0.398	0.334	-0.197
SO_4^{2-}	**0.974**	-0.086	-0.096	-0.013	0.067
Ca^{2+}	-0.044	0.415	0.413	0.683	0.025
Mg^{2+}	-0.071	0.264	-0.074	**0.903**	-0.193
Na^+	0.189	0.115	0.863	-0.152	-0.228
K^+	**0.797**	0.063	0.086	0.236	0.239
HCO_3^-	-0.500	0.558	0.415	0.369	-0.244
As(III)	0.090	0.582	-0.085	**0.756**	0.074
As(V)	-0.080	**0.959**	0.128	0.108	-0.013
Total As	-0.042	**0.943**	0.083	0.287	0.008
E_h	0.486	0.011	-0.110	**0.820**	0.002
pH	0.020	0.049	**0.908**	0.108	-0.068
Conductivity	**0.937**	-0.011	0.245	0.124	-0.131
TDS	**0.935**	-0.010	0.246	0.121	-0.134
Variance/ %	**29.9**	**17.9**	**15.1**	**19.8**	**7.5**

The unconventional FHCC algorithm showed qualitative and quantitative characteristics responsable for the dissimilarities of groundwater samples and association of characteristics at each partition level in the hierarchy.

According to Table 5.2, the analyzed groundwater samples are divided in four partition levels, the first two containing chemical parameters related to the natural enrichment of arsenic in the groundwater. The sample distribution on the four levels is also an expression of arsenic enrichment in the groundwater. The first A_1 group contains samples which exceed TVs in case of As (10 μg l^{-1}). The chemical characteristics associated with this water group are geogenic parameters (F^-, Na^+), anthropogenic and of mixed origin (K^+, SO_4^{2-}, NO_3^-), whose concentration is restricted in the groundwater, but also general characteristics of water such as electric conductivity, TDS and pH. Therefore, besides total content and As speciation, the quality monitoring of groundwater naturally enriched with As should contain the previosly

mentioned hydrogeochemical parameters. The second A_2 group mainly contains water samples with total As concentration lower than TVs, and a single sample (12) with content slightly higher than TVs. However, the degree of belonging is low, therefore this sample could be rather considered as intermediary between A_1 and A_2. The characteristics related to samples of group A_2 are As(V), Mg^{2+}, total As, As(III), HCO_3^-, Ca^{2+}, Cl^-, E_h and PO_4^{3-}. Water samples with As content above TVs (A_1) are further divided into two levels (A_{11}, A_{12}). The chemical characteristics associated with group A_{11} suggest the idea of a possibility for distinction of the group containing water samples naturally enriched with As, by the Na^+ - F^- - pH associations. The A_{12} partition level contains one single sample (1) substantially different from the other ones, by the high content of SO_4^{2-}, NO_3^- and K^+ of anthropogenic origin, by application of fertilizers on the soil.

5.9. Conceptual chemical model of groundwater from the Banat Plain

Based on the hydrogeochemical characteristics of aquifer and chemometric models, a conceptual chemical model was elaborated which describes the natural and anthropogenic pathways of occurance of chemical species in groundwater from the Banat Plain (Fig.5.3). The model presents the appearance of As and F^- from natural sources and NO_3^-, SO_4^{2-}, PO_4^{3-} and K^+ from anthropogenic sources [166]. By silicate hydrolysis and dissolution of carbonates, As species are directly released and results the groundwater with Na^+ - HCO_3^- nature with basic character. These conditions induce the desorbtion of arsenate from clay minerals in the oxidative aqufer. This process takes place at pH around 8.5 [180]. Occurance of PO_4^{3-} in high concentration in groundwater is caused by the use of NPK fertilizers, as anthorpogenic sources, and phosphate rich rocks, as natural sources.

The high PO_4^{3-} content in the groundwater determins a high arsenate content as well, because of the process of ionic exchange in aquifer. The occurance of the dominant $HAsO_4^{2-}$ species is consistent with the E_h (oxidative) – pH (basic) condition in aquifer. The predominant Na^+ - HCO_3^- character of groundwater from Banat Plain is also responsable for the natural occurance of F^- from fluorite (CaF_2). The high levels of NO_3^-, SO_4^{2-}, PO_4^{3-} and K^+ could be related to the use of NPK complex fertilizers.

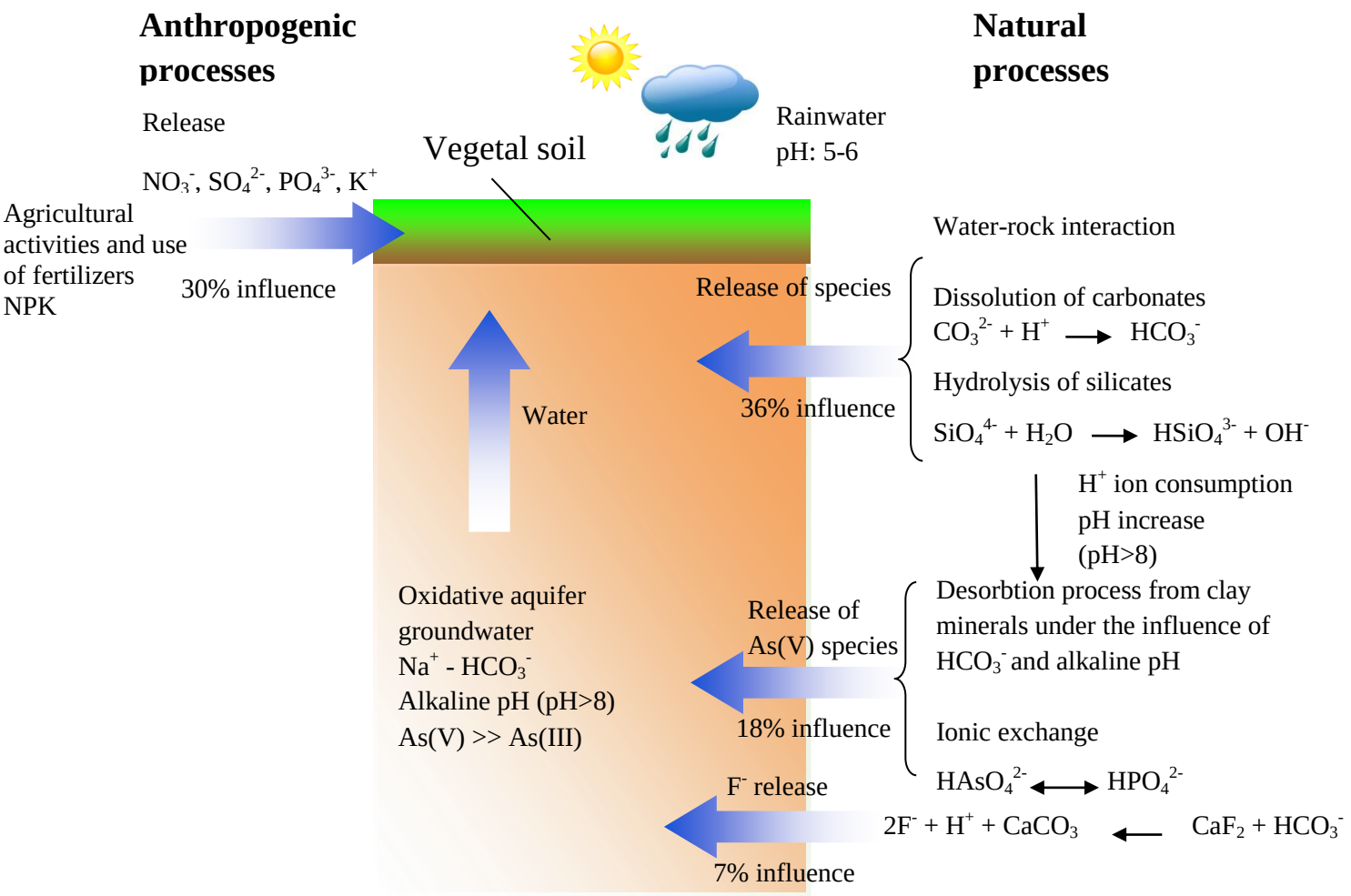

Fig. 5.3. Conceptual chemical model which describes the $Na^+ - HCO_3^-$ nature of groundwater the dominant processes of natural release of As and F^- species and anthropogenic release of NO_3^-, SO_4^{2-}, K^+, PO_4^{3-} in oxidative sedimentary shallow GW-ROBA03 and depth GW-ROBA18 aquifers from Banat Plain [166].

5.10. Conclusions

A model was developed in order to describe the behavior of As species together with other species in the oxidative aquifer of low and high depth from the Banat Plain, by combining unsupervised multivariate chemometric methods like CA, PCA, FPCA and FHCC with classical methods, based on Gibbs, Piper and Stuyfzand diagrams. As a result of the developed model, the chemistry of As was explained together with the high levels of As species and other concomitant species. This methodology offered a deep understanding regarding inorganic As species, anions and cations, as major components in groundwater from Banat Plain, and also described the hydrogeochemical characteristics responsable for aquifer variability. The characteristics of groundwater such as HCO_3^-, PO_4^{3-} and alkaline pH have an important role in the release of inorganic As species from aquifer. Therefore, the water-Ca/Mg rock interaction and the HPO_4^{2-} - $HAsO_4^{3-}$ ionic exchange in aquifer are the main responsable processes for groundwater enrichment with As. The field activities do not influence the concentration of arsenic and F^- species in groundwater from the studied aquifer but lead to the increase of NO_3^-, SO_4^{2-}, PO_4^{3-} and K^+ concentration, as a result of the use of NPK complex fertilizers. The F^- anion appears by a different pathway in comparison with As species, as a result of calcium fluoride dissolution in presence of HCO_3^- and alkaline pH. The PCA statistical approach after the Varimax rotation, as well as FPCA and FHCC demonstarted that the occurance and enrichment of As species in groundwater are caused by natural sources. The F^- - Na^+ - pH cluster was found as a characteristic of groundwater from Banat Plain, with a natural As enrichment. By the FHCC modeling of groundwater with high As concentrations, some characteristics with restricted values were associated, like F^-, Na^+, K^+, SO_4^{2-}, NO_3^-, PO_4^{3-}, electric conductivity, TDS and pH. The FHCC modeling is stronger than CA, PCA after Varimax rotation or FPCA, because it allowed a simultaneous classification and a quick identification of parameters associated with the natural occurance of As in groundwater. From analytical point of view, it was demonstrated that the HG-μCCP-OES method allows the speciation of As as As(III) and As(V) in groundwater and can be successfully used for its characterization.

CHAPTER VI. ORIGINALITY AND NOVEL CONTRIBUTIONS OF THE THESIS. GENERAL CONCLUSIONS

As consequence of the research conducted within the PhD programme, the following original result and innovative contributions were obtained:

1. A modular miniaturized laboratory equipment was developed, based on capacitively coupled plasma microtorch optical emission spectrometry (µCCP-OES) designed for multi-elemental determinations from electrothermally evaporated liquid microsamples, Hg determination after cold vapour derivatization by clasical chemical generation with stanneous chloride solution or by sonication in formic acid medium, and As determination by derivatization to hydride with sodium borohydride in presence of L-cysteine and diluted HCl medium (Fig. 6.1).

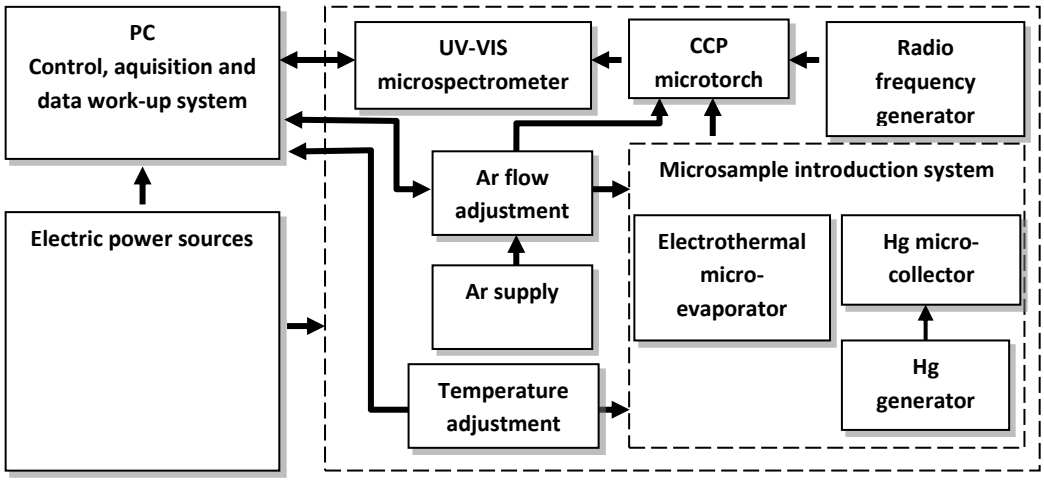

Fig. 6.1. Schematic diagram of the modular µCCP-OES laboratory equipment.

A national invention patent was obtained: 1. Miniaturized analyzer with rhodium filament evaporator for simultaneous determination of elements from liquid microsamples by optical emission spectrometry (131066/30.07.2020) [49]. I am co-author of the present patent.

2. A microanalytical SSETV-µCCP-OES method was developed for multi-elemental determinations for electrothermally evaporated microsamples, applied for Cd determination from foods and As, Ag, Cd, Cu, Hg, Sb, Sn and Zn from soil samples. For the first time, a filament based on Rh was used, which has proved a great advantage by its excellent anti-corrosive resistance. A good capacity of excitation was observed in case of

elements with excitation energies up to 7 eV, obtaining a simple emission spectrum, formed by atomic resonance lines, which constitutes one of the representative characteristics of the method, allowing the use of a low resolution microspectrometer, as alternative of GFAAS and ICP-OES.

3. Two CV-μCCP-OES and SICV-μCCP-OES analytical methods were developed for the determination of mercury from foods and environmental samples, based on cold vapour derivatization by the traditional method in the $SnCl_2$ – HCl system, and by the sono-induced derivatization method in formic acid medium, with or without *on-line* preconcentration of mercury vapours on a gold filament in a microcollector. The methods proved to be viable alternatives of the traditional TD-AAS and CV-AFS used for mercury determination from foods and environmental samples. The absolute novelty of the SICV-μCCP-OES method at international level is represented by the coupling of a sonoreactor with a capacitively coupled plasma microtorch, for the first time.
4. A model was developed which describes the As behavior and characterization of groundwaters from the shallow GW-ROBA03 and depth GW-ROBA18 bodies from Banat Plain, based on As speciation in As(III) and As(V) oxidation states by the HG-μCCP-OES method. The results indicated that both aquifers are oxidative with high natural As content, the major species being As(V). The developed model based on the Gibbs, Piper and Stuyfzand diagrams and the CA, PCA, FPCA, FHCC statistical approaches allowed the identification of groundwater character and chemical processes which explain the As behavior. On statistical basis, the Na^+ - F^- - pH cluster was showed as specific marker for groundwaters with high natural As content.
5. The results were published in seven articles in WOS ranked journals, with impact factor sum of 24.565 and influence factor sum of 9.053, of which three as first author (two Q1 and one Q4).
6. The results were presented at seven international and two national conferences.
7. The μCCP-OES prototype equipment was presented at the national equipment exhibition IRAILF – ROMCONTROLA Bucharest, October 2016.
8. Patent was obtained with the SSETV-μCCP-OES (131066/30.07.2020) instrument [49], and a patent application was handed for OSIM technical evaluation, for the simultaneous microanalytical method for determination of elements from liquid samples with the SSETV-μCCP-OES prototype equipment.

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List of published papers during the Phd programme

Impact factor sum 24.565 and influence factor sum 9.053

Three articles first author: articles 5 and 8 (Q1) and article 6 (Q4)

Crt. Nr.	Article	Impact factor	Influence factor
1.	T. Frentiu, E. Darvasi, **S. Butaciu**, M. Ponta, D. Petreus, R. Etz, M. Frentiu, Application of low-cost electrothermal vaporization capacitively coupled plasma microtorch optical emission sprectrometry for simultaneous determination of Cd and Pb in environmental samples, *Microchem. J.*, 2015, 121, 192 – 196.	Q1 3.594	Q2 1.169
2.	T. Frentiu, **S. Butaciu**, M. Ponta, M. Senila, E. Darvasi, M. Frentiu, D. Petreus, Determinazion of total mercury in fish tissue using a low-cost cold vapor capacitively coupled plasma microtorch optical emission microspectrometer: comparison with direct mercury determination by thermal decomposition atomic absorption spectrometry, *Food Anal. Meth.* 2015, **8**, 643 – 648.	Q2 2.667	Q2 1.065
3.	T. Frentiu, **S. Butaciu**, E. Darvasi, M. Ponta, M. Senilă, D. Petreus, M. Frentiu, Analytical characterization of a method for mercury determination in food using cold vapour capacitively coupled plasma microtorch optical emission spectrometry – compliance with European lregislation requirments, *Anal. Meth.*, 2015, 7, 747 – 752.	Q2 2.596	Q2 1
4.	T. Frentiu, **S. Butaciu**, E. Darvasi, M. Ponta, M. Senilă, E. Levei, M. Frentiu, Sono-induced cold vapour generation interfaced with capacitively coupled plasma microtorch optical emission spectrometry: analytical characterization and comparison with atomic fluorescenvce spectrometry, *J. Anal. At. Spectrom.*, 2015, 30, 1161 – 1168.	Q1 3.498	Q1 1.655
5.	**S. Butaciu**, T. Frentiu, M. Senilă, E. Darvasi, S. Cadar, M. Ponta, D. Petreus, R. Etz, M. Frentiu, Determination of Cd in food using an electrothermal vaporization capacitivelz coupled plasma microtorch optical emission spectrometer: compliance with	Q1 4.258	Q1 1.892

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6.	**S. Butaciu**, M: Ponta, E. Darvasi, M. Frentiu, G. Horvath, T. Frentiu, Development and characterization of a method for the determination of total arsenic in water by hydride generation and optical emission detection in argon capacitively coupled plasma microtorch, *Studia UBB Chem.* 2016, LXI, 299 – 310.	Q4 0.494	Q4 0.036
7.	T. Frentiu, **S. Butaciu**, E. Darvasi, M. Ponta, M. Frentiu, D. Petreus, A microanalytical method base don electrothermal vaporization capacitively coupled plasma microtorch optical emission spectrometry for multielemental determination: comparison with inductively coupled plasma optical emission spectrometry, *Chem. Pap.*, 2017, 71, 91 – 102.	Q3 1.680	Q3 0.531
8.	**S. Butaciu**, M. Senila, C. Sarbu, M. Ponta, C. Tanaselia, O. Cadar, M. Roman, E. Radu, M. Sima, T. Frentiu, Chemical modelling of groundwater, Banat Plaine, Southwestern Romania, with elevated As content and co-occurring species by combining diagrams and unsupervised multivariate statistical approaches, *Chemosphere*, 2017, 172, 127-137.	Q1 5.778	Q1 1.705
	Impact/influence factor SUM	24.565	9.053

List of scientific communications where results of the thesis were disseminated

Crt. Nr.	**International Conferences**
1.	E. Darvasi, T. Frenţiu, **S. Butaciu**, G. Horvath, M. Ponta, S. Cadar, M. Frenţiu, Cadmium and lead determination in environmental samples using electrothermal vaporization from a small-sized Rh coil and detection by capacitively coupled plasma microtorch optical emission spectrometry, The XXIst International Conference of Chemistry, 23 – 27 September 2015, Şumuleu Ciuc, Romania.
2.	M. Frenţiu, E. Darvasi, **S. Butaciu**, G. Horvath, M. Ponta, T. Frenţiu, Mercury determination in food and environmental samples using sono-induced cold vapor generation and detection by capacitively coupled plasma microtorch optical emission spectrometry, The XXIst International Conference of Chemistry, 23 – 27 September 2015, Şumuleu Ciuc, Romania.
3.	T. Frentiu, **S. Butaciu**, E. Darvasi, M. Ponta, M. Frentiu, D. Petreus, Microanalytical Method Based on Electrothermal Vaporization Capacitively Coupled Plasma Microtorch Optical Emission Spectrometry for Multielemental Determination. Comparison with Inductively Coupled Plasma Optical Emission Spectrometry, 43rd International Conference of the Slovak Society of Chemical Engineering, May 2016, Tatranke Matliare, Slovacia, PROCEEDINGS, ISBN: 978-80-89597-35-2, EAN: 9788089597352, pp. 410-419.
4.	S. Cadar, T. Frentiu, E. Darvasi, **S. Butaciu**, M. Ponta, M. Frentiu, D. Petreus, Electrothermal vaporization device for sample introduction in microplasma sources used in elemental determination by optical emission spectrometry, 43rd International Conference of the Slovak Society of Chemical Engineering, May 2016, Tatranke Matliare, Slovacia, PROCEEDINGS, ISBN: 978-80-89597-35-2, EAN: 9788089597352, pp. 420-426.
5.	**S. Butaciu**, T. Frenţiu, E. Darvasi, M. Ponta, M. Şenilă, R. Etz, As, Sb and Hg Determination in soil by electrothermal vaporization and optical emission spectrometry, The 11th Conference ELSEDIMA, May 2016, Cluj-Napoca, Romania.
6.	J. Darvasi, T. Frenţiu, M. Ponta, **S. Butaciu**, D. Petreuş, S. Cadar, M. Frenţiu, Presentation of a Capacitively Coupled Plasma Microtorch Optical Emission Spectrometer Prototype, The XXIIth International Conference of Chemistry, November 2016, Timişoara, Romania.

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National Conferences

1. T. Frentiu, M. Ponta, E. Darvasi, **S. Butaciu**, M. Frentiu, D. Petreus, Protoype microspectrometer for determination of elements by capacitively coupled plasma microtorch optical emission spectrometry with electrothermal evaporator.
   The XXXIVth National Conference of Chemistry, October 2016, Călimăneşti Căciulata, Romania.
2. T. Frentiu, M. Ponta, E. Darvasi, **S. Butaciu**, M. Frentiu, D. Petreus, Prototype microspectrometer for determination of chemical vapour generator elements by OES in capacitively coupled plasma microtorch with electrothermal evaporator. The XXXIVth National Conference of Chemistry, October 2016, Călimăneşti Căciulata, Romania.

Exhibition at IRAILF-ROMCONTROLA Fair, October 2016, Bucharest

1. T. Frenţiu, M. Ponta, E. Darvasi, **S. Butaciu**, M. Frenţiu, S. Cadar, D. Petreuş, D. Şulea, Prototype microspectrometer for determination of chemical vapour generator éléments by capacitively couple plasma microtorch optical emission spectrometry.
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2. T. Frenţiu, M. Ponta, **S. Butaciu**, M. Frenţiu, D. Petreuş, D. Şulea, Prototype microspectrometer for determination of éléments by capacitively coupled plasma microtorch optical emission spectrometry with electrothermic evaporator. IRAILF-ROMCONTROLA National Fair, October 2016, Bucharest, Romania.

OSIM Patent

Crt. Nr.	**Patent**
1.	T. Frentiu, M. Ponta, E. Darvasi, **S. Butaciu**, S. Cadar, M. Senila, A. Mathe, M. Frentiu, D. Petreus, R. Etz, F. Puskas, D. Sulea, Miniaturized analyzer with rhodium filament evaporator for simultaneous determination of elements from liquid microsamples by optical emission spectrometry, No. 131066/30.07.2020