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PhD Thesis

UNCONVENTIONAL ATOMIZATION METHODS IN FLAME AND PLASMA

– ABSTRACT –

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KEYWORDS:

Trace analysis, alkaline metals, electrothermal vaporization, Pt-loop, CCP microtorch

INTRODUCTION

Atomic spectroscopy is one of the oldest instrumental methods having the roots in the spade work of Bunsen and Kirchhoff in the XIXth century. The propelling force in the development of atomic spectroscopy as an analytical technique is the improvements achieved in the design of new spectral sources as well as of optoelectronic instrumentation for signal detecting in order to insure the possibility of multielemental analysis characterized with high precision and sensibility at a low cost.

The laboratory analytical technology used in current analyses is the inductively coupled plasma atomic emission spectroscopy (ICP-AES), whose base was laid in the 1960s. Today ICP-AES is a mature technique capable of exceptional performances by the deployment of spectroscopes with detectors made up of charge coupled device (CCD). One problem which continues to be an impediment in the improvement of such instruments is the miniaturization of the plasma torch and of the spectral sourse of great power.

The advantages of the miniaturized spectral system in comparison with the ICP-AES are: the low consumption of Ar, low power needed for the maintenance of the plasma, the lack of supplementary water-cooling, simple construction of the torch, battery used as power supplier, the simple emission spectrum enables the use of microspectrometers with lower resolution (spectral bandwidth of 0.33–1.5 nm). The excitation capacity of the microplasma is not as good as of the ICP, nevertheless the microtorches have several utilities in the analytical technologies such as specific detectors for gas chromatography as well as for multielemental analysis of liquid microsamples evaporated electrothermally.

Having respect for the present-day trends in the developement of atomic emission spectroscopy the objectives of the thesis are the followings:

1. Elaboration of some atomic spectroscopy methods which enable the trace analysis of three alkaline metals (Li, Rb, Cs) by using miniaturized sample introduction systems for the electrothermally evaporated liquid samples.
2. Implementation of an in situ evaporation system for the methane-air flame characterized with low thermal inertia in order to insure a rapid vaporization of a microprobe with a volume of a few μL and to obtain high sensibility.
3. Optimization of the method for the lithium and cesium determination from mineral water samples and for the rubidium determination from wines, beers, vegetable and fruit squeezes.

4. Establishment of the figures of merit (detection limit, non-spectral effects, matrix modifiers) for the newly developed method versus the classical method of pneumatic nebulization.
5. Verification of the robustness by statistical tests (liniar regression and Bland and Altman test) of the new method in comparison with the pneumatic nebulization, the latter considered as reference technique.
6. Development of a simple and robust method for the determination of lithium from commercialized mineral waters by atomic emission spectroscopy using a capacitively coupled microtorch able to be applied over a wide analyte concentration range as well as a wide multimineral matrix composition of the samples.
7. Verification of the robustness by statistical tests (liniar regression and Bland and Altman test) of the new method in comparison with the standard addition, which is an efficient method in compensating the matrix effects, but extremely laborious.

Li, Rb and Cs are those alkaline metals which are present at trace levels in the environmental samples. Surface waters contain Li in a very low concentration range (1–10 $\mu g\ L^{-1}$). The presence of Li in the potable water is beneficial in overcoming manic-depressive disorders. Lithium salts have been used as drugs in medicine for a few decades. The necessity of monitoring of lithium levels in the blood has lead to the development of sensitive analytical methods for the quantification of lithium from liquid microsamples. The quantification of Cs from mineral waters is of great importance in the geographical classification of these waters. Rb exhibits an important role in the geographical classification of some drinks, namely of wines and fruit squeezes among Li, Mg, Sr, Mn, and has a crucial role in the discovery of wine falsification.

These elements have low excitation energies, so that there is no necessity of complicated instrumentation for their analyses at trace levels. It has been chosen the flame atomic emission spectroscopy for carrying out the analyses as the flame is the most accessible spectral source. The miniaturized sample introducing system enables the vaporization of the liquid microsample which is introduced into the methane-air flame. The spectrometer with the capacitively coupled Ar microplasma has a simpler construction and can be operated at more advantageous conditions than the ICP-AES or r.f.CCP-AES spectrometers. Using this technique a rapid method was developed for the Li determination from mineral waters whithout the necessity of standard addition.

The novelty presented in this thesis is the study of the influence of some matrix modifiers over the kinetics of the electrothermal vaporization process of the analyte. The importance of this study is more outstanding taking into account the capability of these chemical agents to overcome the nonspectral matrix effects as well as to improve the analytical sensibility. The newly developed methods for the Li, Rb and Cs quantification from environmental samples are characterized by simplicity and rapidity. These methods do not require a laborious sample preparation.

The results presented in this thesis were publicated in 3 journals ISI ranked and 2 international conference volumes. A part of the original rezults makes the subject of an article with possiblity of publication in Food Chemistry, where it was sent and is under review. The cumulative impact factor of the published articles is of 2.461.

ORIGINAL CONTRIBUTIONS

The novelties of the research presented in this thesis are the followings:

1. A miniaturized liquid sample introduction system was designed when the flame is used as spectral source. For the first time platinum loop was used for liquid microsample introduction into the methane-air flame for trace analyses of some alcaline metals (Li, Rb şi Cs) by flame atomic emission spectroscopy.
2. The elaboration of a method for compensating the non-spectral matrix effects of the major alcaline- and alcalineearth metals by the use of special matrix modifiers (boric acid, citric acid, acetonoe) constitutes a pioneer work in the field. An increase of about one order of magnitude in sensibility can be achieved with their use. In the presence of these modifiers the evaporation of the analyte is more reproducible and it takes place in the form of a single species.
3. Simple and rapid methods were implemented with success for the quantification of Rb in wines, beers and squeezes, Li and Cs in mineral water samples and Cs in lichens by in-situ electrothermal vaporization of the samples deposited on the Pt loop, the methaen-air flame serving as atomizationand excitation source. The methods are characterized by high sensibility, robustness, simpleness and rapidity without the necessity of a laborious sample preparation process.
4. It was elaborated a method for the quantification of Li in bottled carbonated and degasified mineral waters with different mineral matrices using a capacitively

coupled microplasma as spectral source in atomic emission spectroscopy. The method is based upon the compensation of matrix effects by the addition of a multimineral matrix to the samples and standard solutions. The novelty of the instrumentation is the CCP microtorch which offers the advantage of low Ar and power consumption. This method may be an alternative to the standardized atomic emission spectroscopy methods using the inductively coupled plasma as a spectral source.

1. SPECTRAL SOURCES AND THEIR APLICATION IN THE ATOMIC EMISSION SPECTROSCOPY

In the atomic emission spectroscopy the most frecvently used spectral sources are the flame and the plasma. The role of these spectral sources is to ensure an adecvate medium for the vaporization, atomization and excitation of the analyte.

1.1. The flame as a spectral source

The flame is the most accesible and non expensive spectral source used in spectrametry. In comperison wuth the plasma, the flame is a relatively cold spectral source, its temperature varies between 3000–5000 K. The methane-air flame used in the newly elaborated method in this thesis is one of the coldest flames. The advantage of the low temperature flames consists in the suppression of the ionization processes of the free atoms in the source, process which is the most prominent in the case of alkali metals. Therefore, when analysing alkali metals the sensibility of the AES method can be simply improved by the use of the cold sources.

1.2. Unconventional sample introduction techniques using flames as spectral source

In our days the FAES method has reached maturity. The process which are taking place in the flame are well known and deeply studied, and the techniques are properly suited. The FAES method is applied for the liquid samples which are introduced into the flame by continuous nebulization. Neverthless, the sensibility is is limited by numerous factors: the residence time of the atoms in the flame (is no longer than a few ms), the poor nebulization efficiency (does not exceed 10%), the presence of interferents.

Sensibility may be inhanced by two ways:

– extending the residence time of the free atoms in the flame;

– direct introduction of the liquid or solid sample into the flame, omitting the sample digestion and dilution process.

The in-flame residence time of the atoms can be extended by the use of atom-trapping cells: a device which can be a long-tube atom trap or a slotted-tube atom trap. Considerable improvements in the sensibility can be achieved with such devices [1–9].

The discontinuous sample introduction can be attained by the use of filaments, loops, strips made of different chemically inert metals as Ni, Pt, W, Ta. The pioneer work in this field of research is assigned to Delves who proposed a rapid determination of Pb from a few μL blood sample in the 1970s [10]. The Delves cup made of Ni proved to be an important innovation in the FAAS technique for the volatile elements: Pb and Cd. Such devices were commercialized by the Perkin-Elmer firm.

Several improved models of the Delves cup were proposed. The material of the cup was also changed to steel, ceramic, quartz. More recently researches with filaments, coils of Ta, Pt, W were done. In our days portable microspectrometers were implemented. A comparison of these techniques is summarized in Tabelul 2.1.

Tabelul 1.1. Comparison of the perfomances in FAAS and FAES

Nr.	Technique	Analized elements	LOD	Ref.
1	classic FAAS/FAES	multilelemental	1–100 μg L^{-1}	[23]
2	ETV-FAAS, Delves cup	Cd, Pb	< 0.2 μg L^{-1}	[10]
3	ETV-FAES (filament of Ta)	Li	1.8 μg L^{-1}	[12]
4	ETV-FAES (Pt loop)	Li	0.34 μg L^{-1}	[14]
5	ETV-FAES/FAAS (filament of Ta)	Mn, Pb, Cu, Cd, Li, Na, K	< 0.1 ng	[16]
Portable microspectrometer				
6	FAES	Na, K	100 μg L^{-1}	[20]
7	ETV-FAES (W coil)	multielemental	0.9–8 ng L^{-1}	[21]
8	ETV-FAES (W coil)	Li, Na, K, Rb, Cs	0.5–6 μg L^{-1}	[22]

1.3. Plasmas used in spectroscopy at macro level

The plasma is considered the fourth state of the matter, which is constituted of neutral molecules, free electrons, positive and negative ions. These particles possess high energy and are capable to excite atoms and molecules, to initiate chemical reactions which cannot take place at the ambient temperature. The plasma state is not stable at normal earthly conditions, but it can be evolved artificially and has different applications. Plasmas used in atomic spectroscopy are: direct current plasma (DCP), inductively coupled plasma (ICP), capacitively coupled radiofrequency plasma (r.f.CCP) şi microwave induced plasma (MIP).

1.4. Plasmas used in spectroscopy at micro level

The notion micro is attributed to those devices which have at least one dimension less than 100 μm. In the case of microplasmas the millimetric dimension is equally included [33]. The ICP spectrometers can be operated only in laboratory conditions. In order to miniaturize these apparatus for their use in field works the researches have focused upon the development of microplasmas which can be operated at low power (10–300 W), frequencies of 1–100 and low Ar flow rates (bellow 1 L min^{-1}) [34]. The first generation inductively coupled microplasmas (ICMP) had the following properties: operating power of 0.5–20 W, frequencies of 100–460 MHz, and the diameter of the coil was of 5–15 mm. The plasma could be initiated and operated at low pressure (0.1–10 Torr) [38]. The first stable capacitively coupled microplasma was developed by Platzer and coworkers [37]. The plasma had a length of 20 mm and a diameter less than 1 mm. The plasma was stable only when desolvated samples were introduced in it.

A special advantage of the μCCP in contrast with ICMP is the possibility of operating the plasma at atmospheric pressure. The operation of ICMP plasmas at the same pressure would require extremly high frequency generators, otherwise the torch must be connected to a vacuum pump.

1.5. Unconventional sample introduction techniques using plasma as spectral source

Reaserches in the field of plasma spectroscopy have been carried out in order to develop chemically inert metallic devices (filament, cup, coil) for discrete sample introduction. The technique was first described by Salin and Horlick [63], and is based on the implementation of graphite electrod, or cups and coils made of Ta, Mo or W. These devices enable the analyses of microsamlpes: solid samples of 1–20 mg and liquid samples of about 5 µL can be introduced into the plasma. Tungsten devices were the most studied: tubes, cups strips, filamnets, loops, coils. Karanassios [65, 66] implemented Re loops and cups. Together with Weagant [41, 42] they have miniaturized a sample introduction device used with classic ICP spectroscope for a MPD system. Kim et al. [39] have designed a sample introduction system with a Ta filament for low pressure ICMP.

The r.f.CCP plasma was scarcely investigated in spite of its notable performances. Pless [67] and Anghel [68] analysed electrically conductive samples which constituted one of the electrodes [67], or the powdered sample was introduced into a W cup [26].

2. THE IMPORTANCE AND ANALYSIS OF SOME ALCALINE METALS

The alcaline metals which are present at trace levels in the natural environment are Li, Rb and Cs. In some research fields of geology, biology and medicine their importance is considerable and there is a claim for the analytical techniques and istrumentations which enable their rapid, accurate and robust quantification.

The most sensitive methods for the quantification of lithium are ETAAS and ICP-MS, but the methods based on the atomic emission and absorption in flames are also prefered because of the simplicity of the instrumentation and low-cost operating conditions. ICP-AES is widely used for the rapidity and sensibility of analyses, but the quantification of Rb and Cs traces is difficult because of the intensive ionization processes. ICP-MS is more adequate, when the ICP has the role of the atomization and ionization of the analyte. The quantification of Rb and Cs is prefered with GFAAS, FAES or FAAS methods.

3. MULTIELEMENTAL ANALYSIS OF Li, Rb, Cs BY FAES METHOD FROM ENVIRONMENTAL SAMPLES

3.1. Reagents. Standard solutions and CRM

Monoelemental stock solutions of 1000 mg L^{-1} Li, Na, K, Rb, Cs, Mg, Ca, Sr de concentrație de 1000 mg L^{-1} were prepared of NaCl, KCl, LiCl, RbCl, CsCl salts (Merck, Darmstadt, Germany) by dilution in double distilled water, and of Mg, $CaCO_3$, $SrCO_3$ (Specpure, Johnson Mattey Chemicals Limited, England) by dilution in chlorhydric acid (Merck, Darmstadt, Germany).

Stock solutions of 1000 mg L^{-1} of Cl^{-}, NO_3^{-}, SO_4^{2-} şi PO_4^{3-} were prepared by the dilution of concentrated HCl, HNO_3, H_3PO_4, H_2SO_4 (Merck, Darmstadt, Germany). Stock solutions of 1000 mg L^{-1} of boric acid, citric acid were prepared by dilution of H_3BO_3, $C_6H_8O_7$ (Merck, Darmstadt, Germany) in double distilled water. Acetone (Merck, Darmstadt, Germany), as a matrix modifier was used in its commercialized form.

The accuracy of Li and Rb determination was checked by analyzing a certified reference material for freshwaters (LGC Standards, SRM 1643e Simulated Freshwater-Trace elements) purchased from LGC Promochem GmbH, Germany.

3.2. Sample preparation

The natural mineral water samples were collected in November 2009, in accordance with the EPA prescriptions, from twelve mineral springs in Homorod city area (Harghita County, Romania) and from eight mineral springs in Secuieni area (Bihor County, Romania). The samples (500 mL) were conserved on the spot with 1 mL of conc. HNO_3. Twelve bottled mineral waters were analyzed as purchased from the market. All the samples were stored at $4^{o}C$. The samples were properly diluted with distilled water before analysis. Boric acid was added to the samples in a final concentration of 10 mg L^{-1}.

Carbonated waters were degassed by ultrasonication. Samples were diluted 10-1000 times so that the emission signal for Li falls within the calibration range of the detector and the analyte concentration to be at least three times the detection limit. After sample dilution the multimineral matrix concentration (mg L^{-1}) became: 1.72–92.8 Na, 0.03–4.9 K, 0.12–13.4 Mg şi 0.01–21.7 Ca.

Lithium concentration was determined by the matrix-matching approach (100 mg L^{-1} Na and 100 mg L^{-1} K using boric acid in concentration of 10 mg L^{-1} as matrix modifier) and compared with the result in the standard additions procedure using boric acid as matrix modifier.

In order to determine rubidium, the beers (Ursus, Timis¸oreana, Ciuc, Golden Brau); the red wine assortments (Kadarka, Pinot Noir, Cabernet Sauvignon, Murfatlar Cabernet Sauvignon) from Murfatlar and Dealu Mare vineyard region (Romania), vintage 2005 and 2006; the white wines assortments (Sauvignon Blanc, Ciumbrud blend, “Cure” blend) from Aiud city region (Alba county, Romania), vintage 2006, were analysed as purchased. The fresh fruit and vegetable juices were centrifuged for 10 minutes at 12000 rpm; the supernatant liquid was decanted. All the samples were stored in glass bottles at 4 °C. The samples were properly diluted with distilled water before analysis. Acetone was added to the wines and juices in a final concentration of 5% (v/v) and 10% (v/v) for the beers, respectively.

Rubidium concentration was determined by standard calibration (in the presence of 50 mg L^{-1} K and 5% acetone) and standard additions method (in the presence of 5% acetone).

Cesium concentration was determined in mineral waters collected from springs in the area of Puturos Mountain (Eastern Carpathians). The samples (500 mL) were acidified with 1 mL concentrated HNO_3 so that the pH reached values of 1–2, and were stored in plastic bottles at 4 °C. The lichen samples were collected from the Hasmas Mountains. The samples were dried in oven at 105 ºC and meshed; desegregated by acid digestion at atmospheric pressure using 5 mL concentrated HNO_3 and 5 mL H_2O_2. The solutions were diluted with double distilled water to final volume of 50 mL.

Cesium concentration was determined by standard calibration (in the presence of 100 mg L^{-1} K and 10% acetone) and standard additions method (in the presence of 10% acetone).

3.3. Instrumentation

The measurements were carried out using a single-beam HEATH-701 (Heath Co., Benton Harbor, MI, USA) spectrometer, equipped with a M12FC51 (NARVA, Germany) photomultiplier (900–1100 V). The photomultiplier signal was fed via a homemade A/V converter and a data acquisition card (Decision–Computer International Co. Ltd., USA) into Pentium II PC computer. The data were processed with a home written Q-basic software program language using the boxcar averaging method. The characteristics are listed in Table 3.1.

The fuel gas was the 99% purity methane from pipes; the oxidant was compressed air. The original slot-type burner (for C_2H_2–air flame) was replaced with a similar, Mecker-type, developed for atomic absorption/emission measurements in the M–A flame. The burner was operated at three different airflow rates of 200, 300, 400 L h–1 and at corresponding methane rates of 24, 26; 34, 36; 44 and 46 L h–1, respectively.

The vaporizer (Fig. 3.2), consisted of an Φ = 0.08-mm-diameter 50-mm-long Pt-wire with a 3-mm-diameter loop in the middle. Each end of the wire was fixed in stainless steel tube (hypodermic needles). Electrical cable contacts soldered to these ends assure the connection to a D.C. power supply (TR-9252/A). The whole assembly was fixed in a Teflon disc. The loop was introduced manually into the flame by rotation of the disc in the mounting. Aliquots of 3 µL solutions were injected onto the platinum wire using a 10 µL volume glass syringe, Hamilton 701 N (Swiss–Bonaduz).

The sample was dried by electrical heating of the wire to 120 °C for about 40 s and then it was introduced into the flame by manual rotation of the Teflon head. During atomization, electric heating was maintained. Six replicate determinations were made in each case, the mean, the standard deviation, and S/N were calculated. The peak height values have been considered, using the OriginLab Corporation (Northampton, MA 01060, USA) software package (version 7.0220).

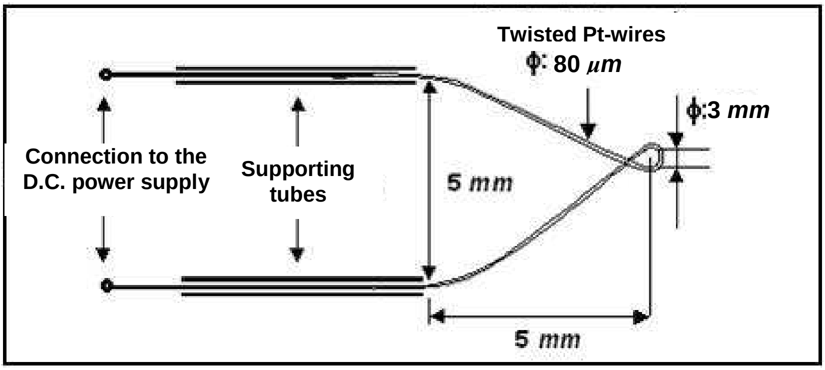

Fig. 3.2. Structure of the Pt-loop vaporizer

Tabelul 3.1. Characteristics of the ETV-FAES system

Units	Characteristic
HEATH EU – 707 Spectroscope	Modular, single-beam
	HEATH EU – 709 Monochromator, linear dispersion of 100 pm at a slit width of 60 μm, and 1000 pm at a slit width of 500 μm
	Detecție cu fotomultiplicator tip M12FC51 (NARVA, Germany) alimentat la -900 – -1100 V
Burner	Mecker type developed for methane-air flame Gas flow rates: 24–46 L h^{-1} (CH_4) and 200–400 L h^{-1} (air)
Sample introduction system	Pt-loop (Φ = 3 mm) formed by two twisted wires (Φ = 80 µm) Mobile teflon head d.c. Power Supply, Type TR-9252/A for electrothermal heating
Sample injection	Glass syringe for chromatography (Hamilton 701 N, Swiss-Bonaduz) Sample volume: 3 μL
Sample drying	Drying temperature: about 120 °C Duration: 30–40 s Current intensity: 1.2 A
Data processing	Acquisition card: Decision-Computer International Co. Ltd., USA Pentium II PC (120 MHz, 32 Mb RAM)
	Processing of data: boxcar averaging method Acquisition speed: 0.33 ms

3.4. Optimization of flame parameters and atomization process

Working parameters (observation height, gas flow rates) were optimized, the influence of alcaline and alcaline-earth metals and of some matrix modifiers over the emission signal was studied.

The variation of the signal-to-noise S/N ratio was plotted against the observation height, measured from the level of the loop with 1 mm steps (Fig. 3.4). The Pt-loop together with the Teflon head was moved in vertical direction by rotating a micrometric screw.

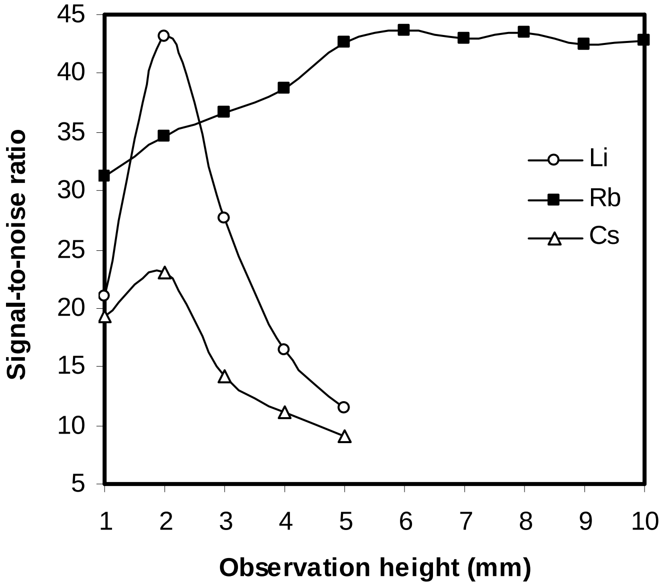

Fig. 3.4. Optimization of the observation height

Tabelul 3.2. Optimum flame and atomization parameters for Li, Rb, Cs

Parametrii	Characteristics		
	Li	Rb	Cs
Wavelength	670.8 nm	780.0 nm	852.2 nm
Air-methane flow rates	300-34 L h^{-1}	300-34 L h^{-1}	200-24 L h^{-1}
Current intensity	1.2 A	1.2 A	1.2 A
Slit width of the monochromator	60 μm	60 μm	500 μm
Observation height	2 mm	5 mm	2 mm
Voltage of the photomultiplier	– 1100 V	– 1000 V	– 1000 V
Sample volume	3 μL	3 μL	3 μL

The optimum observation heights were: 2 mm in the case of Li and Cs, and 5 mm in the case of Rb (Fig. 3.4.). The optimization of the gas flow rates was realized based upon the S/N ratio. The methane flow rate was varied between 200–400 L h^{-1} and that of the air was varied between 24–46 L h^{-1}. The optimum air-methane flow rates were: 300–34 L h^{-1}

for Li and Rb, and 200–24 L h^{-1} for Cs. The optimum flame and atomization parameters are listed in Table 4.2.

3.5. Study of the influence of matrix modifiers

Influence of the major alcaline and alcaline-earth metals (Na, K, Mg, şi Ca) over the emission signal of Li (0.1 mg L^{-1}), Rb (0.5 mg L^{-1}) and Cs (0.5 mg L^{-1}) have been studied in the concentration range of 10–200 mg L^{-1} (Fig. 3.11).

In the case of Li, instead of the increase of the signal, a considerable decrease was observed. The signal reducing effect was more pronounced in the presence of alcaline metals. The decrease of the signal is the consequence of the poor vaporization efficiency, because a great part of the flame energy is consumed in the ionization of the alcaline and alcalin-earth metal halides. The Li signal decreases in the order of the increase of dissossiation energies of the chlorides:

Mg (318 kJ mol^{-1}) < Ca (398 kJ mol^{-1}) < Na (411 kJ mol^{-1}) < K (428 kJ mol^{-1}).

Rubidium and cesium ionize more readily than lithium, thus Na, K, Mg and Ca have ionization suppressing influence upon their emission signal. The most efficient of them proved to be K, in its presence the signal of Rb increased 2 times, and the signal of Cs increased 4 times. Mg has a pronounced signal enhancing influence upon the Cs signal, causing an increase of 5 times when present in 50 mg L^{-1}. This unexpected behaviour of the Mg can be explained by the formation on the loop of a double salt of CsCl and $MgCl_2$, namely carnallite, which has an incongruent melting point at 200 °C [155].

The influence of anions: Cl^-, NO_3^-, SO_4^{2-} şi PO_4^{3-} upon the analytical signal of Li (0.004 mg L^{-1}) was studied. The anions were added in concentrations of 10, 20, 50, 100 and 200 mg L^{-1}. All the studied anions exhibited interference over the Li signal, causing the decrease of it. The decrease was not higher than 18% in the presence of chloride, nitrate and sulphate, but was conciderably higher in the presence of phosphate. When the concentration of the phosphate was in the range of 100−200 mg L^{-1}, the decrease of the Li signal decreased with 34−40%.

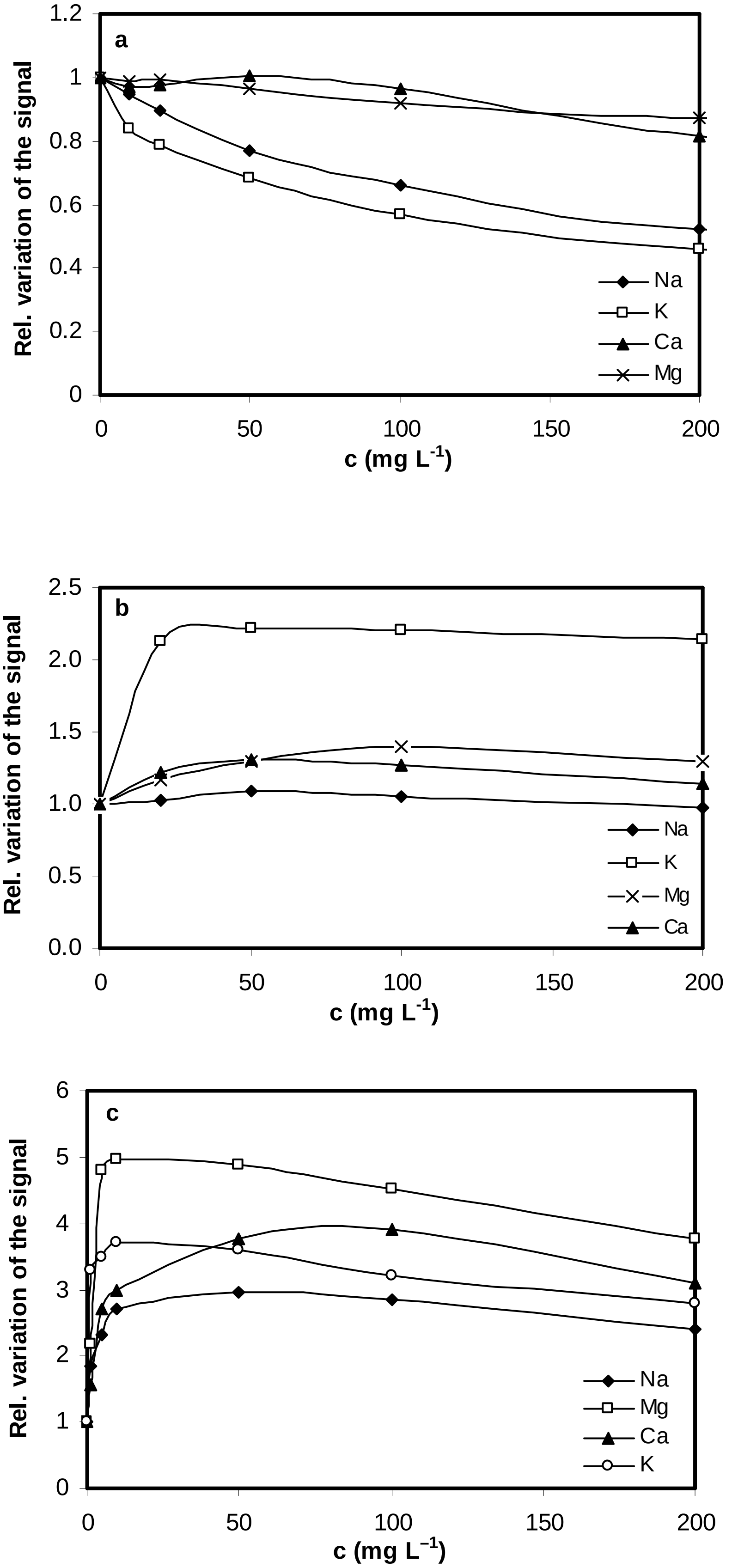

Fig. 3.11. Influance of the alcaline and alcaline-earth metals over the analytical signal of: (a) Li, (b) Rb şi (c) Cs

3.6. Study of some matrix modifier upon the sensibility

When the Pt-loop vaporizer is used as a sample introduction technique into the flame the efficient vaporization of the analyte is crucial. The vaporization and atomization of the analyte can be influenced by matrix modifiers. These are chemical compounds which react with the analyte and change its properties. Some common matrix modifiers, used in electrothermal vaporization were chosen: boric acid and citric acid, both generating oxides from the chlorides of the alcaline metals. Acetone was used as well, as an organic compound miscible with water, which forms complexes with alcaline metals whose melting points are relatively low.

Boric acid

The matrix modifier effect of boric acid upon the emission signal of Li was observed in recording a higher and narrower analytical signal. The benefic influence of the boric acid upon the emission signal of Rb and Cs was also proven. The signals with two peaks recorded in both cases when boric acid was not added to the solutions changed in signals with one peak showing that in the presence of boric acid Rb and Cs evaporates in the form of a single compound (probably the oxides) instead of two. The signal became higher and narrower in both cases.

The influence of the boric acid over the interference of the anions upon the emission signal of Li was tested. Solutions of 0.004 mg L^{-1} Li were preparated with anion concentrations varying between 10–200 mg L^{-1} Cl^-, NO_3^-, SO_4^{2-}, respectively PO_4^{3-}, (preparated from the concentrated acids). The variation of the Li signal against the anion concetrations is shown in Fig. 4.29. The interference of chloride, nitrate and sulphate was completely elliminated. The interference of phosphate was significant when it was present in concetrations higher than 20 mg L^{-1}.

Citric acid

Citric acid was the most efficient sensitivity enhancing agent in the case of Cs. When 100 mg L^{-1} citric acid was added to the Cs solution, a signal enhancement of 6 times was recorded. The Li signal was increased only by 1.4 times, and the Rb signal was increased by 1.2 times. In concetrations higher than 200 mg L^{-1} the capacity of citric acid to increase the analytical signal decreased in each studied case. The relative standard deviations were 1–2.7% for Li, 4–11% for Rb and about 1% for Cs.

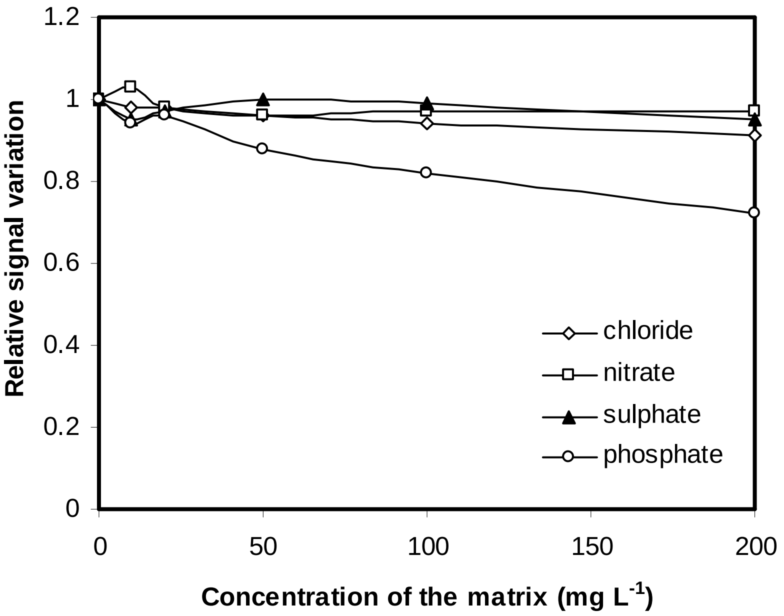

Fig. 3.29. Influence of boric acid and the anions upon the analytical signal of Li

Acetone

Acetone improved the sensibility in the case of Rb and Cs, tha analytical signal increased 1,5 times in the case of Rb and 1,8 times in the case of Cs when acetone was added in concetrations of 5% (v/v), respectively 10% (v/v). The acetone did not enhance the analytical signal of the Li, on the contraty, the Li signal decreased. This behaviour of the Li signal may be the consequence of the greater stability of the Li-acetone complex in comparison with the Rb- and Cs-complexes, and it hardly dessociates in the flame [155].

3.7. Analytical performances

The analytical performances were evaluated by limit of detection (LOD), precision and liniar concentration range.

Lithium

The influence of K, citric acid and boric acid upon the calibration was studied. The liniar concentration range was 0.001–0.1 mg L^{-1}, respectively 3–300 pg. The least limit of detection was obtained when calibration was carried out in the presence of 10 mg L^{-1} boric acid: 0.02 μg L^{-1}, respectively 0.06 pg. This limit of detection is about 3–25 times lower than that obtained with the ICP-AES method [100, 103], and about 10 ori higher than the llimit of detection of the ICP-MS method. In comparison with the methods elaborated for microplasmas, this limit is 50–100 times lower [41, 42, 62].

Rubidium

The influence of K, acetone, citric acid and boric acid upon the calibration was studied. The liniar concentration range was 0.004–1.2 mg L^{-1}, respectively 12–3600 pg. The lowest limit of detection was obtained in the presence of acetone (5%) and K (20 mg L^{-1}), which was 0.4 µg L^{-1}, respectively 1.2 pg. This LOD is 2–10 times lower than the LOD of ICP-AES method [103], and of 10–400 times higher than the LOD of the ICP-MS method. In comparison with the evaporation from a tungsten coil into the oxygen-acetylene flame the LOD is 7.5 times lower [22].

Cesium

The influence of K, Mg, acetone, citric acid and boric acid upon the calibration was studied. The optimum calibration was obtained in the presence of acetone 10% (v/v), with limit of detection of 0.5 µg L^{-1}, respectively 1.5 pg. The liniar concentration range was 0.01–1.0 mg L^{-1} (30–3000 pg).

The LOD is about 10 times lower than the LOD obtained with FAES şi FAAS methods [22, 100, 143], and about 100–250 times higher than the LOD of the ICP-MS method [134, 146].

3.8. Internal validation of the method

Lithium and rubidium concentrations of a certified reference material for fresh waters (SRM 1643e) were determined. The certified values were: 17.4 ± 1.7 µg L^{-1} for Li, and 14.14 ± 0.18 µg L^{-1} for Rb. The confidence intervals were calculated based on the Neyman-Pearson criterion at a significance level of 0.05. Thus the confidence interval for Rb was of ± 0.05 µg L^{-1}, and for Li was of ± 0.03 µg L^{-1} pentru Rb.

The recovery of Li was 100% when calibration in the presence of boric acid was carried out. The recovery of Rb was of 102–103% when standard additions method was carried out in the presence of acetone 5%.

3.9. Determinatin of Li, Rb şi Cs from environmental samples

3.9.1. Determinatin of Li from mineral waters

Li was determined from mineral waters by two methods:

– *newly elaborated method*: standard calibration with matrix matching (Na, K) in the presence and in the absence of boric acid;

– *reference method*: standard additions method by continuous nebulization.

The calibration was carried out in the concetration range of 10–100 mg L^{-1}. The results are listed in Table 3.23.

Little concentration values were obtained in the following mneral waters: Borsec, Dorna, Lithinia, Cheile Bicazului, Izvorul Zânelor, Zizin, Lipova and Bucovina (2–50 μg L^{-1}); medium Li levels characterized the waters: Roua Minunilor, Perla Covasnei, Perla Harghitei, Buziaş, Oaş-Negreni, Odyseus (100–500 μg L^{-1}); and elevated levels of Li (over 500 μg L^{-1}) characterized the Tuşnad and Vâlcele waters (767, respectively 1440 μg L^{-1}). Two mineral waters (Hera, Izvorul Minunilor) had Li concetrations under the LOD of 0.35 μg L^{-1}. The mineral waters from the Homorod springs had medium Li levels (H2, H6, H8, H9, H10, H11 and H12), the concetration varied between 200–500 μg L^{-1}, and four samples had Li concetrations over 500 μg L^{-1}. Comparing the results raported by Schrauzer şi Ohgami [76, 77], it is important to conclude that the mineral waters of Transylvania have elevated Li levels.

In order to verify the applicability of the newly elaborated method statistical analyses were used. The statistical test were: the linear regression method and the Bland and Altman test. The linear regression method showed that the calibration with matrix matching gave significantly different results from the results exhibited by the reference method. At a significance level of 0.05 the confidence interval of the intercept laked the 0 value. The results obtained with the calibration method in the presence of boric acid showed no significance difference from the results given by the reference technique. In this case one can admit that the method is aplicable for the Li determination from mineral waters.

The Bland and Altman test gave similar result with hte linear regression. Based upon the Bland and Altman test one can admit, that the calibration with matrix matching is rejected, on the other hand the calibration in the presence of boric acid is accepted.

Table 3.23. Li concentrations of the water samples (average concentration ± s, n = 5)

Samlpe No.	Pneumatic nebulization	Calibration with matrix matching (Na and K)	Calibration with the addition of boric acid
1	881 ± 18	812.2 ± 3.9	819.3 ± 5.0
2	403 ± 19	392 ± 2.5	375.0 ± 2.7
3	842 ± 18	814 ± 4.7	824.9 ± 5.2
4	753 ± 18	792.7 ± 3.9	757.4 ± 4.3
5	340.0 ± 19	325 ± 2.6	322.8 ± 2.0
6	638.9 ± 18	640 ± 3.1	627.1 ± 3.7
7	308.2 ± 18	287.5 ± 2.4	306.2 ± 1.9
8	219 ± 20	210.7 ± 2.6	194.4 ± 1.4
9	467 ± 19	520.3 ± 2.7	432.9 ± 2.7
10	397 ± 19	411.8 ± 2.3	389.2 ± 2.6
11	384 ± 19	486.3 ± 2.6	376.1 ± 2.7
12	181 ± 21	174.2 ± 5.5	185.7 ± 5.2
13	251 ± 20	244.0 ± 8.3	240.7 ± 6.5
14	1389 ± 23	1338 ± 45	1440 ± 48
15	28 ± 23	33.6 ± 1.1	33.3 ± 1.0
16	136 ± 21	137.5 ± 7.4	152.9 ± 4.1
17	359 ± 18	343 ± 11	355 ± 10
18	22 ± 21	30.5	31.6 ± 0.8
19	276 ± 20	255.3 ± 8.7	245.6 ± 8.1
20	54 ± 17	58.1 ± 1.2	57.0 ± 1.7
21	747 ± 17	713 ± 37	767 ± 17
22	16 ± 11	23.6 ± 0.7	21.1 ± 1.0
23	276 ± 23	338 ± 14	279.5 ± 6.1
24	302 ± 21	312.2 ± 8.8	302 ± 14
25	177 ± 15	168 ± 24	179.0 ± 5.5
26	143 ± 12	183 ± 11	147.6 ± 9.5
27	148 ± 19	134 ± 24	152.4 ± 8.4
28	486 ± 13	497 ± 41	473.9 ± 7.1
29	463 ± 21	454 ± 46	468.8 ± 6.4
30	1878 ± 47	1883 ± 92	1843 ± 20
31	1675 ± 30	1577.1 ± 10	1688 ± 14
32	1123 ± 26	1155 ± 73	1117 ± 12

3.9.2. Determination of Rb from wines, beers and squeezes

The concentrations of rubidium was determined by two methods:

– *newly elaborated method*: calibration in the presence of K and acetone, and standard additions in the presence of acetone;

– *reference method*: calibration and standard additions by the continuous nebulization technique.

The results are presented in Tables 3.27 şi 3.28 [158, 159]. The limits of confidence were calculated at a significance level of 0.05. The Rb concetrations obtained with the calibration method by continuous nebulization in each case were lower than the results obtained with the other techniques. This can be attributed to the presence of polivinilic alcohol present in beers as a foaming agent. This compound modifies the viscosity of the liquid and consequently the nebulization efficiency of the sample. The interference is absent when the sample is vaporized from the Pt-loop.

The results showed, that the red and white wines contain relatively high concetrations of Rb, exceeding 1 mg L^{-1}, and the beers exhibite concetrations around 1 mg L^{-1}. The lowest concetration values were obtained in the case of vegetal and fruit squeezes. The red beet contained unexpectedly high Rb concetration of 2.4 mg L^{-1}.

In order to verify the applicability of the newly elaborated method statistical analyses were used: the linear regression method and the Bland and Altman test. The tests were applied for both the calibration and standard additions methods. It was proven that only the standard additons method can be applied for the Rb determination from wines, beers and squeezes.

Table 3.27. Rb concetrations of the squeezes (n = 5, p = 0.05)

Rb concetration (mg L^{-1})				
Sample	Continuous nebulization		Atomisation from the Pt-loop	
	Calibration	Standard additon	Calibration	Standard additon
Apple	0.38 ± 0.09	0.46 ± 0.05	0.403 ± 0.005	0.42 ± 0.06
Grape	0.89 ± 0.07	0.98 ± 0.09	0.95 ± 0.05	1.16 ± 0.06
Celery	0.46 ± 0.08	0.38 ± 0.09	0.459 ± 0.050	0.51 ± 0.06
Carrot	0.58 ± 0.08	0.66 ± 0.06	0.720 ± 0.007	0.67 ± 0.05
Red beet	1.79 ± 0.08	2.38 ± 0.09	2.376 ± 0.029	2.44 ± 0.06

Table 3.28. Rb concetration of the wines and beers (n = 5, p = 0.05)

Sample	Rb concetrations (mg L^{-1})			
	Continuous nebulization		Atomisation from the Pt-loop	
	Calibration	Standard additon	Calibration	Standard addition
Beers				
Ciuc	0.68 ± 0.06	0.86 ± 0.10	0.90 ± 0.02	1.24 ± 0.11
Golden Brau	0.67 ± 0.06	1.38 ± 0.04	1.10 ± 0.02	1.11 ± 0.12
Ursus	0.62 ± 0.06	1.23 ± 0.10	0.97 ± 0.02	1.35 ± 0.06
Timişoreana	0.73 ± 0.06	1.00 ± 0.08	0.91 ± 0.02	1.15 ± 0.08
White wines				
Sauvignon blanc	1.55 ± 0.31	1.61 ± 0.57	1.71 ± 0.71	1.90 ± 0.02
Ciumbrud blend	0.90 ± 0.4	0.96 ± 0.01	0.88 ± 0.3	1.02 ± 0.09
“Cure” blend	3.39 ± 0.32	3.83 ± 0.12	3.65 ± 0.38	3.89 ± 0.50
Red wines				
Kadarka	1.54 ± 0.02	1.55 ± 0.06	1.585 ± 0.014	1.50 ± 0.09
Pinot Noir	1.41 ± 0.02	1.37 ± 0.3	1.387 ± 0.013	1.38 ± 0.08
Cabernet Sauvignon	2.03 ± 0.02	1.96 ± 0.15	1.491 ± 0.014	1.89 ± 0.16
Murfatlar Cabernet Sauvignon	2.65 ± 0.03	2.07 ± 0.23	2.000 ± 0.019	2.13 ± 0.13

3.9.3. Determination of Cs from mineral waters and lichens

Cesium was determined by calibration (10% and 100 mg L^{-1} K) and standard additions method (10%) based on the peak height and peak area values of the analytical signal [161]. The mean values of three parallel measurements are presented in Tables 3.31 and 3.32. The concentration of Cs in the mineral waters varied between 16–290 µg L^{-1}, and in lichen samples varied between 0.76–5.36 µg L^{-1}.

Two statistical analyses were carried out in order to study the applicability of the calibration method in the presence of acetone and potassium. The standard addition method served as reference method. In accordance with the results of the linear regression and Bland and Altman test the calibration method based either on the peak heigth values or on the peak area values cannot be used for the Cs quantification in mineral waters and lichenThe standard additions remains the reliable method for this purpose.

Table 3.31. Cs concentrations ± u* (µg L^{-1}) of the mineral waters and lichens determined by the standard additions method

Nr. Probă de apă	Înălțime semnal	Arie semnal	Nr. Probă de lichen	Înălțime semnal	Arie semnal
1	84 ± 37	82 ± 44	1	1.28 ± 0.32	1.44 ± 0.16
2	33 ± 12	27 ± 20	2	3.08 ± 1.40	3.64 ± 0.44
3	16 ± 4	26 ± 3	3	0.76 ± 0.32	0.96 ± 0.04
4	31 ± 4	35 ± 15	4	0.96 ± 0.24	1.28 ± 0.24
5	180 ± 80	200 ± 40	5	1.40 ± 0.28	1.52 ± 0.28
6	63 ± 9	71 ± 27	6	1.12 ± 0.44	1.44 ± 0.44
7	250 ± 20	230 ± 20	7	5.36 ± 0.80	6.2 ± 0.04
8	20 ± 4	18 ± 1	8	0.88 ± 0.24	0.84 ± 0.04
9	290 ± 10	270 ± 90			
10	124 ± 40	132 ± 13			
11	41 ± 1	41 ± 1			
12	27 ± 1	30 ± 6			
13	25 ± 2	25 ± 4			
14	27 ± 30	24 ± 16			

u* – confidence limits (n = 3, p = 0.05)

Table 3.32. Cs concentrations ± u* (µg L^{-1}) of mineral waters and lichens determined by the calibration method

Nr. Probă de apă	Înălțime semnal	Arie semnal	Nr. Probă de lichen	Înălțime semnal	Arie semnal
1	83 ± 8	86 ± 12	1	1.8 ± 0.2	2.6 ± 0.3
2	29 ± 2	44 ± 5	2	2.9 ± 0.3	2.9 ± 0.4
3	22 ± 2	27 ± 3	3	1.7 ± 0.2	2.1 ± 0.3
4	44 ± 3	52 ± 9	4	2.5 ± 0.4	2.9 ± 0.4
5	194 ± 18	139 ± 15	5	2.3 ± 0.2	2.2 ± 0.2
6	86 ± 7	75 ± 11	6	1.9 ± 0.2	2.3 ± 0.3
7	264 ± 24	222 ± 20	7	3.4 ± 0.4	4.9 ± 0.6
8	24 ± 2	31 ± 7	8	1.0 ± 0.1	1.6 ± 0.2
9	232 ± 22	315 ± 31			
10	133 ± 13	152 ± 17			
11	35 ± 3	49 ± 3			
12	35 ± 4	32 ± 5			
13	38 ± 4	43 ± 8			
14	35 ± 3	22 ± 9			

u* – confidence limits (n = 3, p = 0.05)

4. DETERMINATION OF LITHIUM FROM MINERAL WATERS BY ATOMIC EMISSION IN A MICROPLASMA

4.1. Reagents. Standard solutions. Certified reference material

Monoelemental stock solutions of 1000 mg L^{-1} Li, Na, K, Ca and Mg as nitrate (Merck, Darmstadt, Germany) were used. For the optimization of the working conditions in μCCP-AES a solution of 5 μg L^{-1} Li was prepared. Solutions containing 1 μg L^{-1} Li in the presence of Na, K, Ca and Mg up to concentrations of 20 mg L^{-1} were used in the study of the non-spectral interferences. The accuracy of Li determination was checked by analyzing a certified reference material for freshwaters (LGC Standards, SRM 1643e Simulated Freshwater-Trace elements) purchased from LGC Promochem GmbH, Germany.

4.2 Sample preparation

A number of 31 carbonated and non-carbonated commercial-bottled-waters were subjected to analysis. According to the product label the mineral matrix (mg L^{-1}) was in the range: 0.75–317 Na; 0-39 K; 3–335 Mg and 9.6–287 Ca. Carbonated waters were degassed by ultrasonication. Samples were diluted 10-1000 times so that the emission signal for Li falls within the calibration range of the detector and the analyte concentration to be at least three times the detection limit. After sample dilution the multimineral matrix concentration (mg L^{-1}) became: 0.01–2.5 Na; 0–0.26 K; 0.05–3.25 Mg and 0.15–6.7 Ca. Lithium concentration was determined by the multimineral matrix-matching approach and compared with the result in the standard additions procedure. In the matrix-matching approach a multimineral matrix of 5 mg L^{-1} Na, K, Ca and Mg was added both in the Li calibration standards (0–5 μg L^{-1}) and diluted samples. In the standard additions procedure three aliquots of diluted samples were spiked as appropriate with 0.1; 0.2 and 0.4 μg L^{-1} Li or 1; 2 and 4 μg L^{-1} Li.

4.3 Instrumentation

The experimental set-up of μCCP-AES previously presented [34] (Fig. 4.1) consisted of a home-made CCP microtorch and radiofrequency generator, commercially available ultrasonic nebulizer and CCD microspectrometer equipped with fiber optic for collecting radiation emitted by the plasma and data processing system. The home-made CCP microtorch is based on a 13.56 MHz Ar plasma sustained at 10–30 W power level on the tip of a Mo microelectrode mounted in a quartz tube (5 mm i.d., 25 mm length, 160 nm cut-off, H. Baumbach & Co Ltd., Ipswich Suffolk, UK). The characteristics of the μCCP-AES system are presented in Table 4.1.

The Ar flow together with aerosol enters the plasma sheath through 0.75 mm diameter holes made on the microelectrode support on a 3 mm diameter circumference. Plasma is ignited by touching the quartz tube with an external grounded electrode after the rf power is connected and arises as a diffuse discharge on the tip of the powered microelectrode. The fiber optic of the microspectrometer is mounted on a XYZ translator with 0.1 mm increment adjustment allowing the choice of viewing zones in plasma. The miniature Ocean Optics microspectrometer is connected to the computer via a universal USB port. The Spectrasuite soft allows the background correction. Lithium signal was measured at 670.776/670.791 nm line cluster.

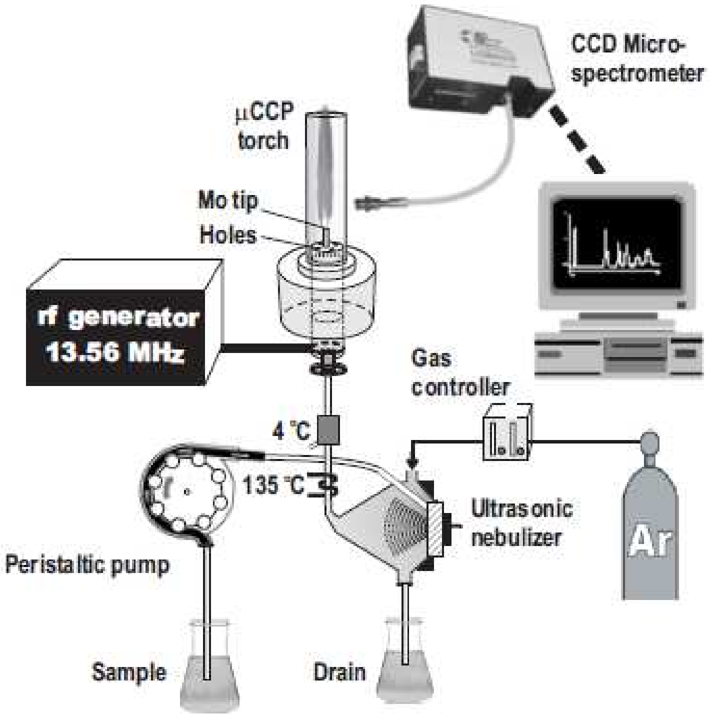

Fig. 4.1. The μCCP-AES system with ultrasonic nebulizer

Tabelul 4.1. Characteristics of equipment used in the μCCP-AES system

Radiofrequency generator	Free-running oscillator, 10–30 W power level, 13.56 MHz (Technical University of Cluj-Napoca, Faculty of Electronics, Telecommunications and Information Technology); dimensions (LxWxH): 15x17x24 cm^3.
Plasma microtorch	Capacitively coupled with central Mo tip microelectrode (1 mm-diameter); 5 mm i.d. quartz tube, 25 mm length, 160 nm cut-off; (INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania); working gas: 5.0 quality argon (Linde Gas SRL, Timisoara, Romania); Ar flow rate: 0.4–0.7 L min^{-1}.
Sample introduction system	Ultrasonic nebulizer (Cetac Technologies, Omaha, USA); heater temperature set at 135˚C; Peltier cooling system set at 3˚C; sample flow rate 1.0 mL min^{-1}.
Detection	HR4000 Microspectrometer Ocean Optics CG- UV – NIR (200–1100 nm, 5 μm entrance slit, Toshiba CCD with 3648 pixels 1304AP, FWHM~1.5 nm, fibre optic QP 600 μm, 25 cm length (Ocean Optics, Dunedin, USA) Collimating fused silica lens (5 mm diameter, 10 mm focal length; beam divergence 2^0 or less; 0.22 numerical aperture of spectrometer collimating mirror).
Data acquisition	Spectrasuite soft (Ocean Optics); 15 - 30 s integration time; background correction: computer-subtracted.

4.4. Optimizarea parametrilor de lucru

The working conditions in the μCCP-AES system were optimized in respect with integration time of signal, Ar flow rate, observation height and power level in order to achieve the maximum signal-to-background ration (SBR). The 20 s integration time of the emission signal ensured the maximum SBR so that all subsequent measurements were conducted under these conditions.

The working conditions established as optimum were: 15 W plasma power, 0.6 L min^{-1} Ar flow rate and a viewing height of 11 mm above the tip electrode.

Study of the matrix effects

Matrix effects were evaluated as the ratio of the Li emission in the presence and absence of the mineral matrix. Concentrations up to 1 mg L^{-1} of any of the four concomitants resulted in an increase of 5–6 times of Li emission. The enhancement of the analyte emission in the presence of low concentrations of alkaline and earth-alkaline elements is explained by the shift of the ionization equilibrium towards the atoms. Rahman and Blades [40] also reported an increase of species density in a CCP torch with parallel-plate electrodes and sample introduction by electrothermal vaporization in the presence of small amounts of EIE, which resulted in a higher number of collisions that made the plasma hotter and hence increased the atom signal. For concomitant concentrations above 2 mg L^{-1} the emission signal in our μCCP remained almost constant (Fig. 4.5). This find was valorized to overcome the matrix problem in Li determination using the calibration curve and addition of a multimineral matrix of 5 mg L^{-1} Na, K, Ca and Mg both in diluted samples and Li calibration standards.

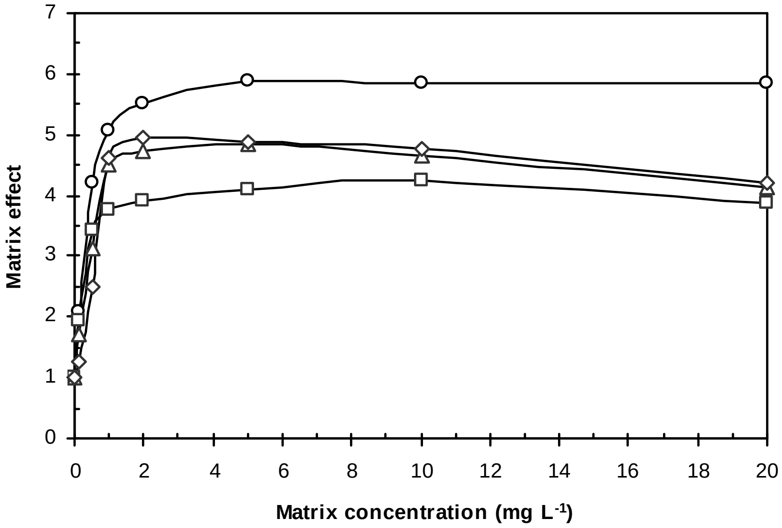

Fig. 4.5. The matrix effect of Na, K, Mg and Ca

4.5. Analytical performances

Calculation of the limit of detection by the methodology of SBR-RSDB

The LOD was determined at the optimum working conditions by measuring both the analytical signal of a Li solution (1 μg L^{-1}) in the presence of 5 mg L^{-1} multimineral matrix (Na, K, Mg și Ca) and the signal of the background. Thus the LOD was of 0.012 μg L^{-1}.

Calculation of the limit of detection by the calibration curve method

The equation of the calibration curve in the range 0-5 μg L^{-1} Li (n = 9) in the presence of 5 mg L^{-1} Na, K, Mg and Ca as multimineral matrix was: Intensity = (2839±84)*c + (2±3) (R=0.9997) for 95% confidence level. The calibration sensitivity of 2839 a.u./ μg L^{-1} and the standard deviation of background (s_b) gave according the 3σ criteria (3 s_b/m) a limit of detection of 0.011 μg L^{-1} Li in μCCP-AES with ultrasonic nebulization. The value of s_b was estimated from 10 successive measurements of the mineral matrix. The detection limit was 230 times better than that reported by us for sample introduction by pneumatic nebulization and 30 W plasma power [34] as well as better than 5 μg L^{-1} or 5 pg Li reported by Weagant et al. [32] using a battery-operated hydrogen microplasma device (MPD) (4 W; 0.25 L min^{-1} Ar-H_2 flow rate).

4.6. Internal validation

The certified reference material SRM 6143e (LGC Standards – Simulated Freshwater Trace-elements) was used for internal validation.

Analysis was carried out using both the standard additions method and the calibration in the presence of the matched-matrix containing 5 mg L^{-1} Na, K, Ca and Mg. The certified value for Li concentration was of 17.4 ± 1.7 μg L^{-1}. The concentration found with the standrad additions method was of 17.3 ± 0.5 μg L^{-1}, and with the calibration method was of 17.2 ± 0.3 μg L^{-1}. In both methods there was a good agreement between found content and certified value. The recovery of the certified mean for 95% confidence level was 99±6% and 99±9% when using the method of standard additions and matrix-matching, respectively.

4.7. Determination of Li from mineral waters

Lithium was determined from 31 bottled mineral waters by the standard addition method and the calibration method in the presence of a multimineral matrix of 5 mg L^{-1} (K, Na, Mg and Ca). The Li concentration of the waters varied on a large scale, the values lied between 0.49–2121 μg L^{-1}.

For the statistic analysis samples were divided in two groups depending on Li concentration, below 100 μg L^{-1} (16 samples) and above 100 μg L^{-1} (15 samples).

According to the parameters of the regression plots and Bland and Altman test there is a good agreement between results obtained by the two methods for 95 % confidence level. For both concentration ranges the confidence intervals of the intercept include the zero value and the slopes are not significantly different from unity. Although the matrix-matching approach provided a better precision (2.5 and 3.5 %) than the standard addition method (3.0 and 6.2 %), the difference between methods was not significant.

The plasma microtorch interfaced with miniaturized CCD microspectrometers, which are now available, is a successful approach for Li determination in drinking water using sample dilution and multimineral matrix-matching.

CONCLUSIONS

As a result of the study of some liquid microsample introduction and atomization techniques in the methane-air flame and in the μCCP argon plasma the following conclusions can be assumed:

1. The implementation of the Pt-loop as sample introduction and atomization device for liquid microsamples used with the methane-air flame in order to determine Li, Rb and Cs traces improves the figures of merit of the FAES technique. The limits of detection were: 0.02 μg L^{-1} Li, 0,4 μg L^{-1} Rb and 2 μg L^{-1} Cs, which correspond to absolute quantities of 0.06 pg Li, 1.2 pg Rb and 6 pg Cs, respectively. In comparison with the classical FAES technique these limits of detection are lower with one order of magnitude. The liniar dynamic ranges were: 0.001–0.1 mg L^{-1} for Li, 0.004–1.2 mg L^{-1} for Rb and 0.01–1.0 mg L^{-1} for Cs. The sensibilities are comparable with the ICP-AES method.

2. Spectral interferences caused by Ca, due to the molacular bands of CaOH and CaO superposing on the atomic line of Li in the spectrum could be overcome by eliminating Ca from the vaporized sample as the melting points of its oxides, chlorides and nitrates are much higher than those of Li. It was proved, that the Ca salts remained on the loop in the short time (2 seconds) when atomization of the analyte took place in the flame.

3. Supplimentary informations over the vaporization process of liquid microsamples in the presence of matrix modifiers (acetone, boric acid, citric acid) were obtained. Boric

acid and citric acid are commonly used matrix modifiers in the electrothermal vaporization technique. Acetone forms complex compounds with alkali metals. The use of these compounds in order to compensate matrix effects was useful and efficient. Boric acid proved to be the most efficient in the determination of Li when the non-spectral interferences caused by chloride, sulphate and phosphate were diminished and the sensibility considerably increased by generating the Li2O instead of LiCl. The former has lower dissociation energy than the latter. The most adequate matrix modifier for Rb and Cs was acetone, by the formation of volatile complex compounds in the drying step. In the case of Cs acetone contributed to the increase of the sensibility. Citirc acid was efficient only in the case of Cs, and improved the sensibility of the method.

4. Lithium quantification in mineral waters with very different mineral contents can be carried out by calibration method with matrix matching (Na and K), using boric acid as matrix modifier in a concentration of 10 mg L^{-1}. The applicability of the method was varified with statistical analyses: linear regression and Bland and Altman test. The determination of Rb in wines, beers and squeezes was carried out by calibration in the presence of acetone 5% and K as ionization suppressor agent, and by standard additions method in the presence of aceton 5%. The statistical analyses showed that only the standard additions method is reliably aplicable.

5. The calibration method and standard additions method were statistically compared in the Cs determination in mineral waters and dezagregated lichen samples. Both the calibration and standard additions method were carried out by addition of acetone (10%) to the standard solutions and diluted samples. Additionally potassium (100 mg L^{-1}) was used as ionization suppresing agent when calibration method was carried out. The statistical tests showed significant diffrence between the calibration and standard additions method at a confidence level of 95%. The Cs determination in mineral waters and lichens is reliable by the standard additions method.

6. The μCCP argon plasma was used for the determination of Li traces in mineral waters. Ultrasonic nebulization followed by deslovation was applied as sample introduction technique. The optimum working conditions were as follows: signal integration time of 20 s, the power of the plasma of 15 W, argon flow rate of 0.6 L min^{-1}

and observation height of 11 mm over the Mo tip. The Ar served as sample carrier and plasma sustaining gas.There was no need of torch cooling.

7. The figures of merit of the method are: the limit of detection calculated on the base of 3σ criterion was of 0.011 μg L^{-1}, the linear dynamic range lies over three order of magnitude (0.01–9 μg L^{-1}). The limit of detection is 100 times lower than the LOD obtained with the same system by using pneumatic nebulization, and is at the same level as the LOD obtained by the Pt-loop FAES technique. The low power of the plasma (15 W) and low argon consumption (bellow 1 L min^{-1}) make possible the design of a portable instrument.

8. Influence of major alkaline- and alkaline-earth metals (Na, K, Mg, Ca) was studied over the emission signal of Li. The metals act as ionization suppressors, causing a signal increase of about 4–6 ori. The enhancement is the result of another phenomenon: in a CCP torch with parallel-plate electrodes and sample introduction by electrothermal vaporization in the presence of small amounts of EIE, it takes place an increase of species density which results in a higher number of collisions that make the plasma hotter and hence the atom signal increases. In the concetration range of 0.1–2 mg L^{-1} the presence of each metal lead to the increase of the analytical signal. At higher metal concetrations the signal became almost constant.

9. Calibration in the presence of a multimineral standard (5 mg L^{-1} Na, K, Mg, Ca) was studied against the standard additions method in order to determine Li in bottled mineral waters. According to the parameters of the regression plots and Bland and Altman test there is a good agreement between results obtained by the two methods for 95% confidence level. The developed method is robust and easy-to-run and can be applied for Li determination in drinking water over a wide concentration range both of analyte and Na, K, Ca and Mg matrix.

10. Both the sample introduction and atomization from the Pt-loop into the methane-air flame and the μCCP-AES method using ultrasonic nebulization followed by desolvation are reliable and sensitive techniques for the Li determination in mineral waters with concentrations as low as 10–20 ng L^{-1}.

PERSONAL PUBLICATIONS

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