Quantification of the Rubidium in Beverage Products Micro Samples by Platinum-wire Loop in Flame Atomization Atomic Emission Spectrometry

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Abstract

The rubidium content in 3 μL of some beverage products (beer, wine, vegetable and fruit juices) atomized from a Pt-wire in the methane-air flame has been determined by atomic emission spectrometry. The flame atomization conditions of rubidium were optimized, they are: $\lambda = 780.0$ nm, the height of 8 mm over the burner head, gas flow rates of 300 L h^{-1} air and 34 L h^{-1} methane. The effect of Na, K, Cs, Sr and acetone on the emission of rubidium was studied too. The limit of quantification (6σ) obtained is of 4.3±1.8 pg in the presence of 50 mg L^{-1} K and 5% v/v acetone (P = 0.05). The rubidium content of the samples has been determined with continuous nebulization and by atomization from the Pt-wire, using the standard calibration curve and the standard addition method. The results of the two procedures agree within the determination errors.

Keywords: FAES, rubidium, platinum-wire, beverages

1. Introduction

Rubidium is a relatively rare lithophile metallic element with a crustal abundance of 78 mg kg^{-1}. It enters easily in living organisms, being considered a non-toxic and biologically non-essential element. The rubidium content of wide range of samples of different origin is quantified using various instrumental analytical methods, as: in plants by instrumental neutron activation analysis (INAA);[1] in honey, wine and natural waters by flame atomic emission spectrometry (FAES).[2–5] AAS was preferred for the determination of rubidium in bones and biological fluids[6–8] and in soils,[9–11] assuring low detection limits of 2.3–20 μg L^{-1} or 24 pg, respectively.[3,5,11] The plasma-based techniques (ICP-AES and ICP-MS) are also suitable for rubidium determination in foodstuffs and soils.[12–14] The nondestructive X-ray fluorescence methods were used in the case of edible fish muscles EDXRF;[15] and soils XRF[16], respectively. Non-spectroscopic methods have been applied too: capillary zone electrophoresis (CZE);[17] and HPLC.[18]

For routine, everyday analysis FAES is preferred as a fast, robust method. The main features of the flame photometers are the continuous run, low liquid throughput (4–8%), significant sample (2–4 mL) and high gas consumption. The detection limits for many metals, including rubidium, are not sufficiently low for many of present-day analysis. These disadvantages are overcome by the evaporation/atomization of few microliter of liquid sample from a high melting point, chemically inert solid surface, as graphite, tantalum, tungsten, platinum. The heating of the device takes place in the flame or by electric current passing through it, placed in an inert gas atmosphere.[19–26] Common features of such atomizer are the intermittent run, high heating rate, chemical inertness, higher sensitivity and lover detection limits (at least one order of mag-

nitude) but poorer stability comparing with continuous nebulization. The platinum in-flame atomizers withstand to few hundred of firings even in oxidative environment, allow high heating rate in cooler flames, up to its melting point of 1772 °C.[23,24] It is possible to quantify elements in the low temperature flames (propane-butane-air, methane-air etc.) with low detection limits, comparable with hotter flames.[27]

2. Experimental

2. 1. Instrumentation

The measurements were carried out at the atomic line of $\lambda = 780.0$ nm using a single-beam HEATH-701 (Heath Co., Benton Harbor, MI, USA) spectrometer, equipped with a M12FC51 (NARVA, Germany) photomultiplier (–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.[28] 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.[27] The atomizer, consisted of an $\Phi = 0.08$-mm-diameter 50-mm-long Pt-wire with a 3-mm-diameter loop in the middle. The device used is the same described in details elsewhere.[29]

2. 2. Procedure

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).

2. 3. Chemicals

Stock standard solutions of Rb, Cs, Na, K and Sr were of 1000 mg L^{-1}, prepared from RbCl, CsCl (Merck, Darmstadt, Germany), NaCl, KCl (Reactivul, Bucureşti, Romania), SrCO$_3$ (Specpure, Johnson Matthey Chemicals Limited, England), by dissolving the appropriate amount in double distilled water and in HCl (analytical grade, Merck, Darmstadt, Germany) respectively. For further dilutions, double distilled water was used. Acetone (analytical grade, Reactivul, Bucureşti, Romania) was added to each calibration and sample solutions.

2. 4. Sampling and Sample Handling

The beers (*Ursus, Timişoreana, 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.

3. Results

3. 1. Optimization of the Flame and Atomization Parameters

The emission of 6 ng of rubidium in the M–A flame was observed in the flame up to d = 18 mm over the burner head (in 1-mm steps) using six different pairs of gas flow rates, the atomization height was 5 mm over the burner head (in the interconal zone of the M-A flame).[27] The optimum experimental conditions characterized with the lowest signal to noise ratio are: gas flow rates of 300 L h^{-1} air and 34 L h^{-1} methane (fuel lean flame), the RSD(%) = 4.5%. Similar behaviour has been registered in the case of continuous nebulization into the M-A flame.[5]

3. 2. Calibration Curves and Detection Limits

The analytical figure of merit of the method was evaluated based on limit of detection (LOD), precision and dynamic linear range at the optimized flame and atomization parameters. The LOD was determined using 6σ at P = 0.05. The calibration has been performed in the concentration range of 0.004–1.0 mg L^{-1}. The calibration curves are linear up to 600 pg of analyte atomized. The presence of acetone in the solution enhances the analytical signal without modifying the linear dynamic range. Admixing K up to a final concentration of 50 mg L^{-1} to the calibration solutions the slope of the calibration curves increases, the linearity is extended to the whole concentration domain. The lowest detection limit of 4.3±1.8 pg was found in the presence of acetone (5% v/v) and of K (50 mg L^{-1}).

3. 3 Interferences

The effect of Na, K, Cs and Sr on the emission signal of 1 mg L^{-1} rubidium was investigated, up to 200-fold

excess. Na and K are present in beverages in higher concentrations; the mineral content could act as evaporation inhibitor of the analyte in the solid phase. K, Cs and Sr are the most efficient ionization suppressors for rubidium. The relative intensity enhancement of the rubidium emission signal versus the concentration of the interferences is represented in Fig. 1.
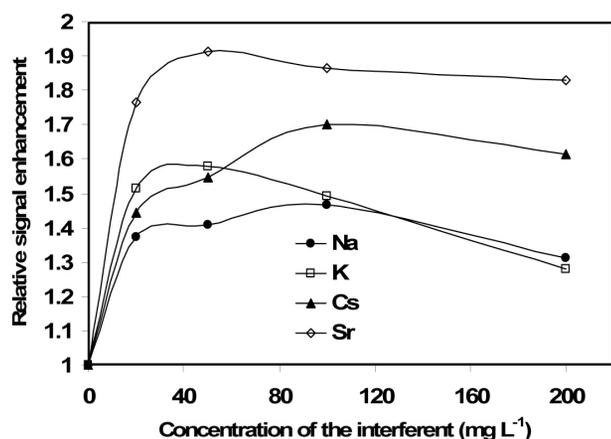

Fig. 1: The relative intensity enhancement of the 3 ng rubidium emission signal versus the concentration of the interferents

The studied elements, up to of 50 mg L^{-1} (except Cs), enhance the emission signal of Rb, mainly due to the ionization suppressing effect. The most efficient ionization sup-

pressor was Sr, by enhancing the signal about 1.9 times. Over 100 time excess of the interferent they hamper the evaporation of the analyte from the platinum surface, being considered as condensed phase interference. Each alkaline metal form stabile, volatile metal ion–acetone– water clusters in solutions, which exist even in the solid phase.[30–32] So acetone could act as matrix modifier, by increasing the analyte volatility in the solid phase. The effect of acetone on the emission signal of 1 mg L^{-1} of rubidium was tested, by adding anhydrous acetone to the Rb standard solution, in 4 steps, with the final concentration of 20%. Acetone enhances the emission signal until 5% v/v of concentration (with about 19%), the RSD% of the determinations at this acetone concentration being the lowest, of 4.1%.

3. 4. Analyses of the Beverage Samples

The rubidium content of the beverage samples has been determined by continuous nebulization and by evaporation from the platinum wire. The standard calibration and the standard addition methods, as the reference one, were used in all cases. Five parallel measurements were made in each case. By the use of the standard addition method 200 µL of concentrated rubidium standard of 0.1 mg L^{-1} was added, in three steps, to the 5 mL of sample. The results are summarized in Table 1.

The results show a good agreement between data; they lie within the errors of the determinations despite of atomization and calibration method used (exception red beet). The standard addition method offers the most repro-

Table 1: The rubidium content of the beverages (n = 5, P = 0.95)

Sample	Rb content (mg L^{-1})			
	Continuous nebulization		From Pt-wire atomization	
	By standard calibration	By standard addition	By standard calibration	By standard addition
Beer				
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 wine				
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 wine				
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
Juices				
Apple	0.38±0.09	0.46±0.05	0.403±0.005	0.42±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	1.68±0.06	1.88±0.09	2.645±0.024	2.58±0.05

ducible results, being closer to real rubidium content of the samples. The close values suggest the absence of the interferences, the methods allow the direct determination of rubidium content of beverages without any prior chemical pretreatment. In the case of beers, the data for continuous nebulization and by standard calibration are systematically lower then those obtained with other procedures, due to the presence of the foaming agent of polyvinyl alcohol (PVA), added to the beers.

4. Conclusions

The optimal atomization height over the burner head is 8 mm and gas flow rates of 300 L/h air and 34 L/h methane, respectively. The presence of K, Na, Cs and Sr, increases the emission signal until 50 mg L^{-1}, than depletes it due to evaporation inhibition. Acetone acts as matrix modifier at 5% (v/v) by increasing the emission signal about 19%. The emission-concentration relationship is linear in the 0–600 pg range in the presence of potassium and acetone, the detection limit is of 4.3±1.8 pg of rubidium. The rubidium content of different beverage samples can be determined precisely by simple dilution with distilled water and by using either the standard calibration curve or the standard addition method. The results of two procedures agree within the determination errors (except beers), being suitable for the direct determination of rubidium in beverage microsamples.

5. References

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Povzetek

Z uporabo atomske emisijske spektroskopije s plamensko atomizacijo z uporabo platinske zanke smo doloèili vsebnost rubidija v 3 µL vzorcih pijaè. Optimizirali smo pogoje atomizacije: λ = 780,0 nm, vi'ina 8 mm nad gorilcem, pretok plina 300 L h^{-1} zraka in 34 L h^{-1} metana. Preuèili smo tudi vpliv Na, K, Cs, Sr in acetona na emisijo rubidija. Meja doloèitve (6σ) je 4,3±1,8 pg v prisotnosti 50 mg L^{-1} K in 5% v/v acetona (P = 0.05). Vsebnost rubidija v vzorcih smo doloèili s kontinuirnim razpr'evanjem in atomizacijo z uporabo platinske zanke, na podlagi umeritvene krivulje kot tudi metode standardnega dodatka. Rezultati obeh metod se ujemajo v okviru eksperimentalne negotovosti.