

ULTRASONIC NEBULISER, A USEFUL TOOL FOR IMPROVING THE SENSIBILITY OF TRACE ELEMENT DETECTION IN SURFACE WATER

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Abstract. In order to analyse trace elements from surface water, drinking water and wastewater an analytical method using Ultrasonic Nebuliser USN U5000AT⁺ equipment coupled with ICP-EOS Optima 5300 DV Perkin Elmer Spectrometer has been developed. Quality parameters (LOD, LOQ) allow the detection on sensitivity level imposed by European Legislation. Optimised parameters for simultaneous determination of Cd, Cr, Cu, Co, Ni and Pb in the range 1 to 5 µg/l were: power setting of 1400 W; auxiliary gas of 0.2 l/min; nebuliser gas of 0.75 l/min; sample uptake rate of 1.9 ml/min; plasma gas rate 15 l/min. Quantification limits obtained using fortified blanks indicated low values such as: 0.075 µg/l (Cd, Co); 0.10 µg/l for (Ni, Pb); 0.15 µg/l (Cr, Cu). The use of an USN as sample introduction system instead of Meinhardt Classic Nebuliser improves LOQ more than 10 times.

Keywords: ultrasonic nebuliser, ICP-EOS, metals, simultaneous determination, water quality.

AIMS AND BACKGROUND

In terms of maximum permissible limits of metal content in water samples (drinking, mineral, surface water, wastewater), limits imposed by the laws, the analytical methods applied must comply from point of view of performance characteristics. Directive 2013/39/EU (Ref. 1) is a restrictive legislation and refers to the approval of the measures against pollution caused by chemical substances. European Directive lays down the environmental quality standards for water, provides for updating the list of priority substances. The regulated data give the maximum allowable concentrations of each substance, set up to avoid irreversible consequences of acute short-term exposure for an ecosystem. Very low detection and quantification limits and high accuracy and precision are required for a performant method for metals analysis². The most appropriate methods are those that apply techniques such as: ICP-MS, USN-ICP-EOS, ET-AAS and SFA. The studies conducted in the literature show that using ultrasonic nebuliser (USN) for metals analysis leads

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to lower detection limits, increasing signal compared with background noise when the ultrasonic nebuliser is attached to an optical emission spectrometer with inductively coupled plasma, simultaneous determination and axial viewing^{3,4}. It was found that use of such equipment leads to considerable improvement of the signal (greater than 10 to 133 times) than using a classic cyclone chamber coupled with Meinhard nebuliser. This increase in signal compared to background noise is approximately 86 times, the limit of detections decreases 6 times, but the quality of environmental conditions are very important in order to avoid contamination during work and improving detection limits⁴. Using ultrasonic nebuliser requires no sample concentration, which decreases their time preparation, but acidification and filtration are required in order to obtain the total concentrations of metals and to inject samples without turbidity in the nebuliser system⁵.

Extensive comparison studies were carried out in the literature on ICP-MS spectrometer coupled either with ultrasonic nebuliser (U5000 AT⁺, Cetac Technologies) or Cross-flow nebuliser, Meinhard/MicroMist nebulisers in order to optimise the metals determination in waste leaching⁶. Comparative studies carried out using different types of pneumatic nebulisers attached to conventional chambers and ultrasonic nebuliser coupled with desolvated membrane shows increased performance of USN-ICP-EOS (Ref. 7). Also, there is information included about the effects of matrix (Ca, Mg, Na, K) in different operating conditions of the plasma and the optimum operating conditions (plasma, auxiliary and nebuliser flows) are set for the type of spectrometer used⁷. Ultrasonic nebuliser is widely used in analytical chemistry. Coupled either with ICP-EOS or ICP-MS, is used to determine the metal content from liquid^{8,9} and solid⁷ environmental matrices, for biological environmental studies (mushrooms collected from metal polluted areas)¹⁰, air dust pollution control^{5,11} or food samples¹². Ultrasonic nebuliser is also used for the determination of pharmaceutical compounds in environmental samples¹³ and volatile organic compounds¹⁴. Another application of ultrasonic nebuliser coupled with ICP-MS spectrometer is the determination of platinum in body fluids (blood, plasma), as result of anti-carcinogen drug administration (Eloxatin) in order to determine the exposure of the body to platinum¹⁵.

Even if the equipments are different and also the applied technique, many studies were performed on the same type of USN, namely U5000 AT⁺ (Cetac Technologies) or the upgraded version with desolvated membrane (U6000 AT⁺, Cetac Technologies)¹⁶⁻¹⁹.

The aim of the study was to develop and validate a method for simultaneous determination of Cd, Cr, Cu, Co, Ni and Pb in water samples using an USN-ICP-EOS spectrometer in order to achieve the imposed limits of the European legislation.

EXPERIMENTAL

Apparatus. Ultrasonic Nebuliser type U5000 AT⁺ Cetac Technologies coupled with an Optima 5300 DV Perkin Elmer ICP-EOS Spectrometer (USN-ICP-EOS), axial viewing plasma; Milli Q water Purification System with Q-POD Element for trace element analysis.

Quality control and assurance. Only ultra-pure analytical grade quality reagents were used. Certified Reference Material solution for calibration (100 mg/l Multi Element Standard Solution, Certipur, Merck), ultra-pure nitric acid (65% Merck quality), argon 99.996% purity, nitrogen 99.99% purity (Linde-Gas quality), ultra-pure water was used for all aqueous solutions and cleaning procedures. The quality control of the data was carried out according to Quality Control Standards 21A, 100 mg/l, produced by Perkin Elmer.

Setting the operating parameters. Establishing optimum conditions for the USN-ICP-EOS was performed using a 'continuous graph' option that allowed maintaining the values of some parameters while peristaltic pump uptake flow and the nebuliser argon rate were modified. Plasma Argon rate and auxiliary rate were established according to the instructions of ultrasonic nebuliser, parameters that are without influence on the signal intensity. In the experimental studies it was observed that a higher power (1400 W power compared to 900 W, respectively 1250 W, as stated in U5000 AT⁺ ultrasonic nebuliser application notes), allows the obtaining of higher intensities.

While the peristaltic pump rate was maintained constant, nebuliser flow varied between 0.5 and 0.75 ml/min and the maximum intensity obtained was noted. The peristaltic pump flow was swept from 1.5 to 2.0 ml/min. The tests were performed at two different concentration levels, 3 and 30 µg/l, respectively. For each element were tested different wavelengths in order to establish the most sensitive one. According to the experimental results, the optimum wavelength for determination of selected metals using USN-ICP-EOS are presented in Table 1.

Table 1. Optimum wavelength with the highest intensity

Metal	Wavelength (nm)	Metal	Wavelength (nm)
Cd	228.802	Cu	228.616
Co	324.752	Ni	231.604
Cr	283.563	Pb	224.688

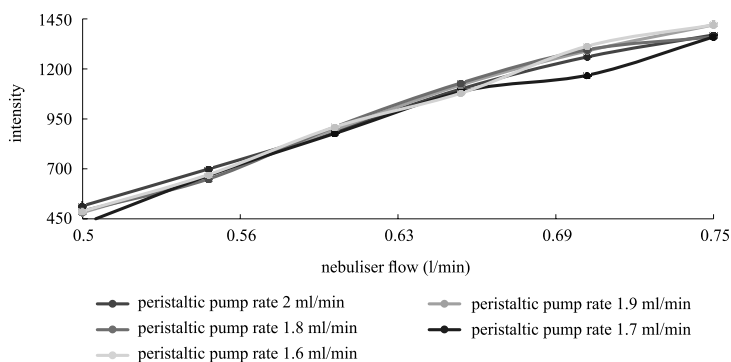
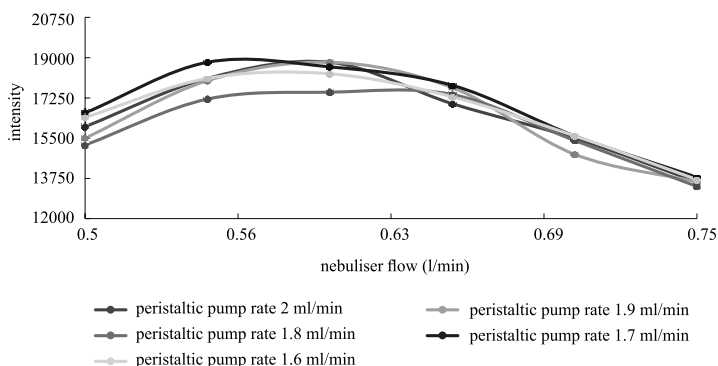
Validation of the method. Validation experiments were performed in the study in order to evaluate the performance of the method (limit of detection LOD, limit of quantitation LOQ, repeatability, intermediate precision) in the range from 1 to 5 µg/l for the simultaneous determination of metals (Table 2).

Table 2. ‘In-house’ validation experiments

Parameters	Experiments
LOD and LOQ	5 independent fortified blank solutions (0.4 $\mu\text{g/l}$)
Repeatability	10 independent standard solution of 3 $\mu\text{g/l}$ concentration
Intermediate precision	4 experiments (3 standard solution per experiment analysed by 2 chemists in 4 different days), 12 independent standard solution of 3 $\mu\text{g/l}$

RESULTS AND DISCUSSION

The intensity values were plotted as a function of nebuliser gas rate at a specific peristaltic pump flow (sample uptake). Some of the experimental data are presented (Cd, Cr, Co), in Figs 1–6. Thus, in Figs 1, 3 and 5 can be observed that at a low concentration level, higher nebuliser flow increases intensity more than sample uptake rate, in order to obtain better sensitivity. In Figs 2, 4 and 6 experimental data performed at 30 $\mu\text{g/l}$ are presented. In these figures it can be observed that both tested parameters (sample uptake rate and nebuliser flow) affect the signal intensity.

**Fig. 1.** Optimised condition for Cd determination ($\lambda = 228.802$ nm, 3 $\mu\text{g/l}$)**Fig. 2.** Optimised condition for Cd determination ($\lambda = 228.802$ nm, 30 $\mu\text{g/l}$)

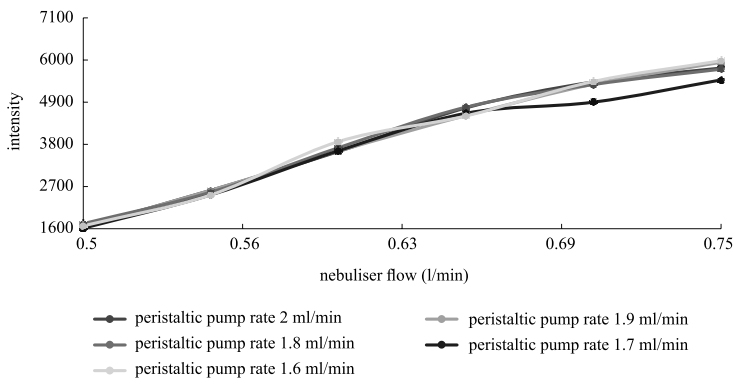


Fig. 3. Optimised condition for Cr determination ($\lambda = 283.563$ nm, 3 $\mu\text{g/l}$)

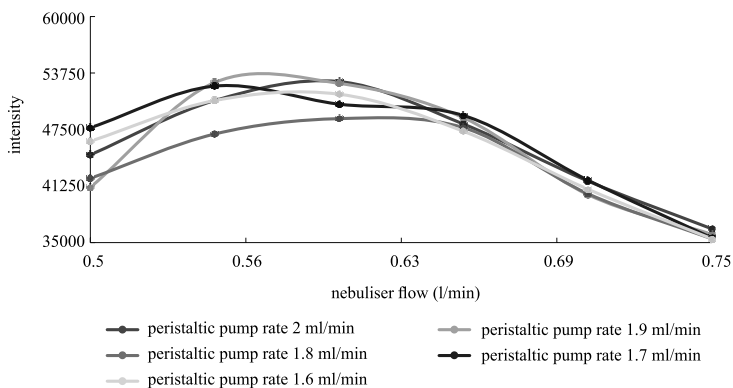


Fig. 4. Optimised condition for Cr determination ($\lambda = 283.563$ nm, 30 $\mu\text{g/l}$)

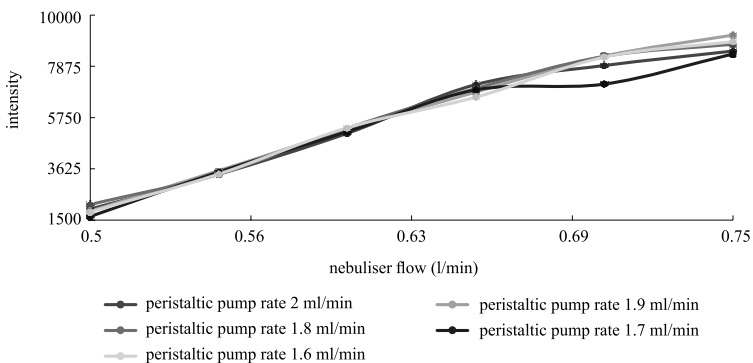


Fig. 5. Optimised condition for Cu determination ($\lambda = 324.752$ nm, 3 $\mu\text{g/l}$)

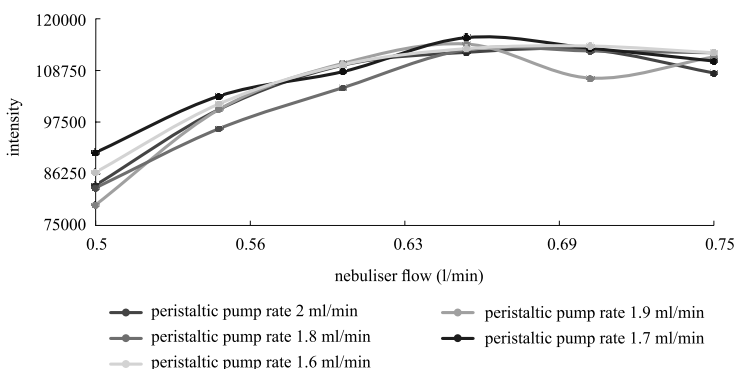


Fig. 6. Optimised condition for Cu determination ($\lambda = 324.752$ nm, 30 $\mu\text{g/l}$)

In Table 3 optimum operating conditions for simultaneous determination are presented (Cd, Co, Cr, Cu, Ni, Pb) in the range from 1 to 5 $\mu\text{g/l}$, parameters obtained at 3 $\mu\text{g/l}$ using ‘continuous graph’ option. In Table 4 the sample uptake and nebuliser flows optimum values for U5000 AT⁺ coupled to ICP-EOS Optima 5300 DV Perkin Elmer spectrometer at 30 $\mu\text{g/l}$ are presented. These parameters could be used for methods applied in the range 10 to 50 $\mu\text{g/l}$.

Table 3. Optimum operating parameters for simultaneous determination (1–5 $\mu\text{g/l}$)

ICP-EOS Spectrometer parameters	
Plasma gas rate (argon)	15 l/min
Auxiliary gas rate	0.2 l/min
Nebuliser gas rate	0.75 l/min
Sample uptake rate (peristaltic pump)	1.9 ml/min
Power RF	1400 W
Number of replicates	4
Delay	60 s
Aria integration	10 points
U5000AT ⁺ UN	
Heater temperature	140°C
Cooler temperature	3°C

Table 4. Sample uptake rate and nebuliser flow at 30 $\mu\text{g/l}$

Metal	Nebuliser gas rate (l/min)	Sample uptake rate (ml/min)
Cd	0.55	1.7
Co	0.55	1.9
Cr	0.55	1.9
Cu	0.65	1.9

In order to compare the limit of detection (LOD), limit of quantitation (LOQ) and accuracy obtained with the implemented method (Table 6), in Table 5 the values

for these characteristics are listed according to Directive 2013/39 / EU¹ and the Romanian Government Decision 1038/2010 (Ref. 20).

Table 5. Limits imposed by the European legislation

Metal	Unit	Maximum admissible value (MAV)	LOD	LOQ	Accuracy
Cd	µg/l	0.25	0.025	≤ 0.075	≤ 0.025
Co	µg/l	0.7	0.07	≤ 0.21	≤ 0.07
Cr	µg/l	2.5	0.25	≤ 0.75	≤ 0.25
Cu	µg/l	1.3	0.13	≤ 0.40	≤ 0.13
Ni	µg/l	4	0.40	≤ 1.20	≤ 0.40
Pb	µg/l	1.2	0.12	≤ 0.36	≤ 0.12

Table 6. Values obtained for the validated method

Metal	Unit	LOD	LOQ	Repeatability	Intermediate precision	Accuracy
Cd	µg/l	0.024	0.075	0.33	0.39	0.02
Co	µg/l	0.02	0.07	0.10	0.40	0.02
Cr	µg/l	0.04	0.14	0.22	0.25	0.07
Cu	µg/l	0.05	0.16	0.38	0.52	0.12
Ni	µg/l	0.03	0.10	0.36	0.37	0.11
Pb	µg/l	0.03	0.11	0.30	0.35	0.07

The limit of detection, limit of quantitation and accuracy (Table 6) are within the limits imposed by the most restrictive law in the European legislation, so the method is suitable for water quality control. In Table 7 detection limits obtained with ICP-EOS Optima 5300 DV Spectrometer (with or without USN) are included. The data show that Ultrasonic Nebuliser as sample introduction system instead of Meinhardt Classic Nebuliser improves LOD more than 10 times.

Table 7. Comparison of LOD on Optima 5300 DV ICP-EOS

Metal	Classic Meinhardt nebuliser (µg/l)	USN U5000AT ⁺	
		experimental (µg/l)	literature (µg/l)
Cd	0.15	0.024	0.03
Co	0.14	0.02	0.04
Cr	0.50	0.04	0.02
Cu	0.40	0.05	0.05
Ni	1.00	0.03	0.04
Pb	2.00	0.03	0.40

Analysis of Cd, Co, Cr, Cu, Ni, Pb in real surface water samples. Using the developed analytical method was performed a study concerning the determination of Cd, Co, Cr, Cu, Ni and Pb in 20 surface water samples collected in April 2015 from

different points situated on Danube River, from Bazias to Saint George Harbour (Table 8). The obtained results are presented in Table 9.

Table 8. Locations of the surface water samples on the Danube River

Sampling point	Location	Sampling point	Location
SW1	Bazias	SW11	Silistra
SW2	Gura Vaii	SW12	Isaccea
SW3	Calafat	SW13	Tulcea
SW4	Rast	SW14	Nufaru
SW5	Bechet	SW15	Balteni
SW6	Ialaz	SW16	Mahmudia
SW7	Turnu Magurele	SW17	Murighiol
SW8	Giurgiu	SW18	Uzlina
SW9	Oltenita	SW19	Ivancea
SW10	Calarasi	SW20	Sfantu Gheorghe

Table 9. Results obtained on surface water samples

Metal	Unit	SW1	SW2	SW3	SW4	SW5	SW6	SW7	MAV*
Cd	µg/l	<0.075**	0.084	0.128	0.120	<0.075	0.131	0.140	0.25
Co	µg/l	0.35	<0.04	0.24	<0.04	<0.04	<0.04	<0.04	0.7
Cr	µg/l	1.50	<0.75	8.55	2.11	1.90	1.85	0.82	2.5
Cu	µg/l	3.02	1.84	3.41	1.92	1.95	2.32	1.60	1.3
Ni	µg/l	8.47	4.05	29.5	9.60	8.91	8.76	2.68	4
Pb	µg/l	2.94	1.94	3.27	1.96	2.13	1.83	2.00	1.2
Metal	Unit	SW8	SW9	SW10	SW11	SW12	SW13	SW14	MAV*
Cd	µg/l	<0.075	0.147	0.080	<0.075	0.096	<0.075	0.090	0.25
Co	µg/l	<0.04	<0.04	<0.04	0.05	0.06	<0.04	<0.04	0.7
Cr	µg/l	<0.75	<0.75	<0.75	0.79	1.16	<0.75	<0.75	2.5
Cu	µg/l	1.92	2.03	2.06	2.14	2.79	1.87	1.90	1.3
Ni	µg/l	3.11	2.44	2.75	2.19	4.92	2.55	1.98	4
Pb	µg/l	2.00	1.80	2.07	2.27	2.67	1.81	1.93	1.2
Metal	Unit	SW15	SW16	SW17	SW18	SW19	SW20	MAV*	
Cd	µg/l	<0.075	<0.024	<0.024	<0.024	<0.024	<0.024	0.25	
Co	µg/l	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.7	
Cr	µg/l	0.75	<0.75	<0.75	<0.75	<0.75	<0.75	2.5	
Cu	µg/l	2.13	2.10	1.01	2.03	2.07	1.87	1.3	
Ni	µg/l	3.03	1.42	1.35	1.64	2.09	2.63	4	
Pb	µg/l	2.07	1.97	1.12	1.96	2.05	1.72	1.2	

* According to Directive 2013/39 / EU¹ and the Romanian Government Decision 1038/2010 (Ref. 20); ** LOQ.

The experimental data show that the results of Cu, Ni and Pb contents in some sampling points are over the maximum admissible value according to Directive 2013/39/EU (Ref. 1). It was observed that the concentrations are higher in Danube when entering into Romania than are in monitoring points from Danube Delta.

Quality of Danube River is monitored in different studies, beginning with the water of the River in Bazias (first monitoring point in Romania), on the way to its flow into the sea (Danube Delta, Sulina, Saint George)^{21,22}. Danube water is used as a source of raw water in order to produce drinking water in some big cities such as Calarasi, Braila and Tulcea.

CONCLUSIONS

The paper presents an optimised and validated method for the simultaneous detection of metals using an ultrasonic nebuliser system connected to an inductively coupled plasma optical emission spectrometer with axial view (USN U5000AT⁺ Cetac Technologies coupled with ICP-EOS Optima 5300 DV Perkin Elmer Spectrometer). The method has performance characteristics suitable for water quality control, the most restrictive law is the one concerning the quality of surface water. Methods applied for drinking and mineral water quality control, as result of maximum admissible limits and performance characteristics imposed, allow the use of an ICP-EOS with a classical sample introduction system. In terms of surface water quality, very low limits require more sensitive methods. The method was verified on different real water samples and the results were included in the acceptable concentration limits.

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