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VALIDATION OF AN ION CHROMATOGRAPHIC METHOD FOR DETERMINATION OF HEAVY METALS IN WATER

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An ion chromatographic method for the simultaneous determination cations of transition metals (Pb(II), Cu(II), Cd(II), Co(II), Zn(II), and Ni(II)) in wet depositions is proposed. An ICS3000 Dionex system equipped with an isocratic eluent delivery pump, isocratic derivatisation reagent pump and WTV molecular absorption detector was employed in evaluating the method performances. The method proposed proved selective, calibration curves are linear in the 50 – 500 µg/L concentration range, characterized by correlation coefficients of 0.999 for each metals of interest. The limits of detection (LOD) and limits of quantification (LOQ) were calculated from the standard deviation of the response and varied in the 0.9 – 6.8 µg/L and 1.3 – 11.8 µg/L concentration range respectively. Repeatability and intermediate precision tests gave RDS% between 0.08 % and 2.95 %, values significantly lower than the imposed limit. The method was tested on wet depositions collected in the Bucharest urban area in December 2012 - March 2013 time interval, giving realistic information on urban atmospheric pollution.

Keywords: method validation, meteoric waters, IC

1. Introduction

The validation of analytical methods is a key concern in all areas of chemical analyses to ensure conformity with national and international regulations.

By validation a method confirms that the analytical procedures used for a specific test is fit for purpose and validation results can be used to evaluate the quality, reliability, and consistency of analytical results. Planning the validation study requires identification of relevant performance parameters and defining the acceptance criteria. The laboratory should decide which performance parameters need to be characterized for validating a method, taking into account the customer

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requirements, existing expertise, and the compatibility requirements with other similar methods used in the laboratory or in third party laboratories.

The precipitations studies were focused on the determination of anions and alkali and alkali-earth cations, the chemical interactions, the distribution of precipitation, the sources of components in wet depositions (marine source, terrestrial source, and anthropogenic source) and meteorological variation [1, 2, 3, 4, 5,6].

IC has become the recommended method for routine analysis in laboratories over the world, being lately complemented by the determination of transition and lanthanide metal ions by chelation ion chromatography. Monitoring of aqueous samples by IC represents a fast, small volume sample demand, and reliable method for determination of transition metals (Fe, Pb, Cd, Cu, Co, Ni, and Zn), being also used for determination of analytes with multiple stable oxidation states [7].

Metal ions can exist in several different forms; in many samples are present as hydrated species, but they also exist as oxy-anions depending on the complexation extent and oxidation state. Hydrated and weakly complexed transition metals can be separated as cations. By adding a strong chelating agent to the eluent, the net charge on the metal is reduced, since the agent is anionic in solutions. The so-called "*mixed mode* separation" is due to the different degrees of association between the metals and the chelating agents producing different net charges on the metal complexes. For higher concentration levels, the metal complexes net charge can be negative. When oxalic acid based eluents are used as chelating agent, ferric ions will not elute.

The need to provide accurate and reliable results enforce laboratories to practice quality management systems according to the EN ISO 17025 standard and engage in method validation projects before shifting new or renewed procedures towards routine exploitation [7,8]. Therefore an ion chromatographic procedure for the simultaneous determination of lead, copper, cadmium, cobalt, zinc and nockel is being proposed, optimized and validated to ensure transfer to routine usage in the monitorization of these ions in the meteoric depositions.

2. Experimental

The equipment used was an ICS 3000 Dionex ion chromatographic system composed of an isocratic eluent delivery pump, isocratic derivatisation reagent pump, CS5 separation column, WTV molecular absorption detector, and an AS40 autosampler.

The IonPac CS5A column displays cation and anion exchange capacity, allowing metals to be separated as cations or anions on a single column. The analytical column was guarded by a CG5A guard column.

The metals were detected by measuring the absorbance at 530 nm of the complex formed with the 4-(2-pyridylazo)resorcinol (PAR) metal complexing reagent.

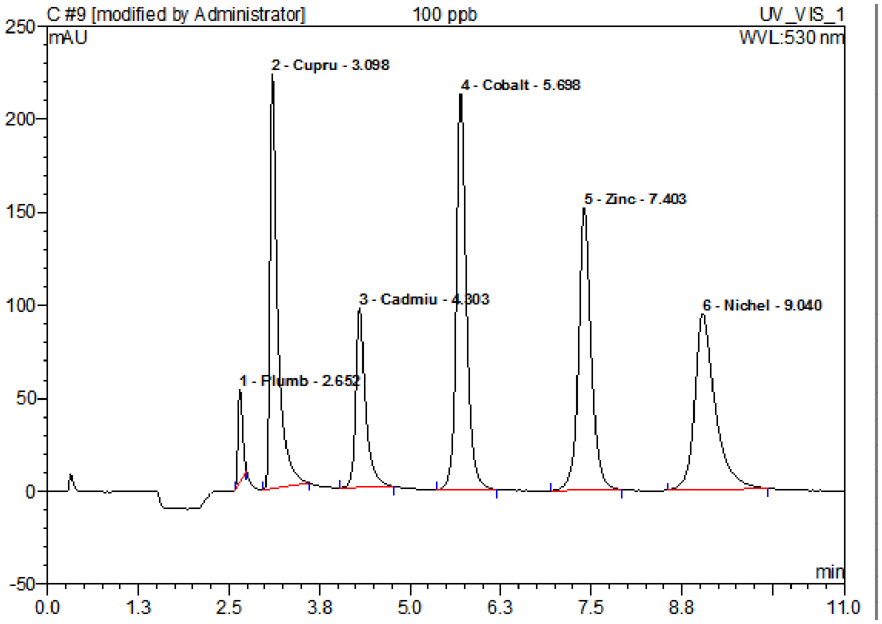

Fig. 1. Typical chromatogram for a 100 µg/L standard solution

The derivatisation reagent was prepared by dissolving a certain amount of PAR (0.06 g for concentration bellow 500 µg) in 1.0 L of the MetPac Postcolumn Diluent. The PAR reagent is added after the separation column, to form a light-absorbing complexes with the transition metal ions. Diluent urchased from Dionex, containing 2–dimethyl aminoethanol (1.0 M), ammonium hydroxide (0.50 M) and sodium bicarbonate (0.30 M) and stored under an inert gas.

The eluent contained oxalic acid (0.008 M), tetramethylammonium hydroxide (0.010 M), and potassium hydroxide (0.005 M). The final pH was 9.2.

All experiments were carried out in the isocratic mode, at 30°C, using optimized operation conditions: 1.2 mL/min eluent flow rate, 0.8 mL/min derivatisation reagent flow rate, 1000 µL injection volume, and a 375–mL knitted reaction coil.

Ultrapure water, 18.2 ΩM/cm, free from all ions to be determined, vacuum degassed, and filtered through a 0.20 µm pore membrane, produced by a TDK system was used for preparing standard solutions.

All calibration standard solutions were prepared by diluting the certified concentration stock standard solutions for ion chromatography containing Pb(II), Cu(II), Cd(II), Co(II), Zn(II), and Ni(II) traceable to SRM NIST (Fluka, Germnany).

The volumetric glassware used for standard solutions preparation was class A**.**

Snow samples were collected from six points in Bucharest using a homemade polyethylene sampler, further treated with HNO_3 (99.99 % purity), and stored in sterilized dry containers at 4°C. Aliquots were used for spiking standard solutions during the method validation procedure and to evaluate the ionic content in wet depositions.

Data processing was carried out with Microsoft Office sotfware.

3. Results and discussion

The selectivity was evaluated by examining the relative standard deviation (%RSD) of the retention times for 12 injections set at six different concentration levels, in the 50 – 500 µg/L concentration range. The average retention times and relative standard deviations are collected in Table 1. In all cases, the relative standard deviation is less than 1 %, so the method can be declared selective, proving that the separation is achieved.

Table 1.

Method selectivity (%RSD)

Analyte	Retention time (min)	*s* (min)	RSD (%)
Pb(II)	2.65	0.005	0.17
Cu(II)	3.09	0.011	0.37
Cd(II)	4.30	0.003	0.26
Co(II)	5.68	0.034	0.60
Zn(II)	7.38	0.005	0.54
Ni(II)	9.01	0.067	0.75

Proving the selectivity of a chromatographic method asks for checking the resolution of the components. Chromatography resolution (R_s) is measured by the parameters which defining the chromatographic peak (retention times and peak width). A good separation between two incompletely separated components, resolution must be at least 1 – 1.5 minutes. The calculated values, shown in Table 2 indicate a good separation of peaks at all concentration levels investigated.

Table 2.

Method selectivity (R_s)

	R_s (min)					
	50 µg/L	80 µg/L	100 µg/L	150 µg/L	200 µg/L	500 µg/L
Lead - Copper	3.09	3.08	3.08	3.17	3.16	3.06
Copper-Cadmium	6.03	6.18	6.18	6.49	6.51	6.70

Cadmiu - Cobalt	6.09	6.21	6.20	6.32	6.13	5.80
Cobalt - Zinc	6.43	6.57	6.43	6.41	6.19	5.63
Zinc – Nickel	4.27	4.26	4.25	4.23	4.14	3.65

The calibration curves were obtained for each analytes of interest at the same time. The concentration ranges, covering the maximum contaminant levels in potable water, were set to 50 – 500 µg/L for lead, copper, cadmium, cobalt, zinc, and nickel (fig. 2).

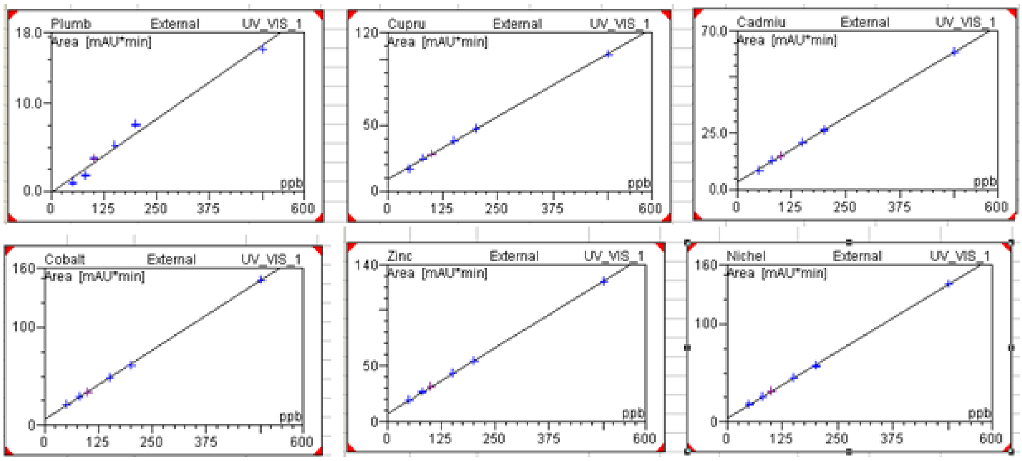

Fig. 2. Calibration curves for Pb(II), Cu(II), Cd(II), Co(II), Zn(II) and Ni(II) recorded with an ICS 3000 equipment

Experiments run at six concentration levels, using two replicate injections for each concentration level gave linear fits for all ions in terms of peak area, characterized by slopes between 0.03 and 0.30 with standard deviations, s_b, of 0.01 – 0.15, intercepts between 0.1 and 9.0, and intercepts standard deviations s_a, between 4.0 and 32.0 (Table 3). Examination of standard residuals demonstrated the lack of outliers for all six calibration curves.

Table 3.

Regression analysis results for the calibration curves

Cation	Slope (b)	Slope standard deviation, (s_b)	Intercept (a)	Intercept standard deviation (s_a)	Correlation coefficient (R^2)	Response standard deviation (s_y)
Pb(II)	0.03	0.01	0.098	3.93	0.999	6.22
Cu(II)	0.19	0.09	9.05	22.32	0.999	35.15
Cd(II)	0.11	0.06	3.22	13.52	0.999	21.30
Co(II)	0.28	0.02	5.81	31.28	0.999	49.27
Zn(II)	0.23	0.12	7.73	27.57	0.999	43.43
Ni(II)	0.27	0.13	3.77	32.00	0.999	50.40

The accuracy test checks the expected result for the analyte peak against the actual result and it is expressed as a percentage (e.g. % bias) determined from at least 2 replicates. The tests were performed on deionised water samples spiked with increasing levels of ions standard solution. The bias values in Table 4 vary within the –3.52 – 7.25 % range. The ± 5% bias condition is fulfilled only starting from 80 µg/L concentration level, so the method is considered accurate only in 80 – 500 µg/L concentration range.

Table 4.

Method accuracy

Cation	50 µg/L	80 µg/L	100 µg/L	150 µg/L	200 µg/L	500 µg/L
Pb(II)	-3.52	-2.48	1.39	5.83	1.54	-2.43
Cu(II)	-14.31	4.40	1.41	1.61	0.55	-0.26
Cd(II)	-13.12	3.21	2.07	1.32	0.59	-0.25
Co(II)	7.22	1.17	-1.44	0.19	-2.57	0.34
Zn(II)	1.42	1.22	-0.55	0.45	-1.24	0.13
Ni(II)	3.69	0.46	-0.19	0.17	-1.66	0.21

The detection and quantification limits were calculated either using the blank standard deviation, s_{blank}, the residual standard deviation of the calibration curve, $s_{y/x}$ and the standard deviation of intercept characteristic to the regression line, s_a. Results collected in Table 5 show different values, depending on the chosen strategy. Limits obtained from the blanks are lowest in the set, varying from 2.27 to 6.45 µg/L for LOD, and from 6.90 to 19.5 µg/L for LOQ. Detection limits estimated from standard deviation of the calibration curve ($s_{y/x}$) present almost equal values for all six metals: 3.60 – 3.90 µg/L, from LOQ and 7.60 – 8.70 µg/L from LOQ range.

LOD and LOQ values calculated from the standard deviation of intercepts provide the larger values for all six metals: while LOQ of 5.74 – 7.92 µg/L, and LOQ within the11.04 – 11.78 µg/L range. Given the increased similarity between the distribution of intercepts and the lowest detectable concentration values, the calculation based on the standard intercept deviation provides more statistically reliable results.

Table 5.

Method detection limit and quantification limits

	LOD [mg/L]			LOQ [mg/L]		
	Blank standard deviation	Calibration data (intercept)	Calibration data (line)	Blank standard deviation	Calibration data (intercept)	Calibration data (line)
Pb(II)	1.47	7.92	3.89	3.58	11.78	8.63
Cu(II)	1.06	6.11	3.87	2.36	11.74	7.94
Cd(II)	1.37	6.84	3.79	3.17	11.75	8.10
Co(II)	0.94	5.74	3.64	1.32	11.04	7.69

Zn(II)	1.29	6.73	3.77	3.27	11.75	8.50
Ni(II)	1.18	6.50	3.38	2.85	11.10	7.61

The repeatability test, checking the consistency of calculated results for the analyte peak over a short time period, by the same user, on the same instrument are collected in Table 6. The relative standard deviations of the peak areas vary between 0.08 and 2.95, all fulfilling the requirements derived from the Horwitz equation at the employed concentration levels, namely RSD $< 2^{(1-0.5\lg c)} =$ 9.6 %.

Table 6.

Method repeatability

Cation	No. of replicates	50µg/L		100µg/L		200µg/L	
		s [µg/L]	RSD [%]	*s* [µg/L]	RSD [%]	*s* [µg/L]	RSD [%]
Pb(II)	10	0.66	2.37	0.59	0.61	0.54	0.19
Cu(II)	10	0.66	1.52	0.59	0.19	0.54	0.10
Cd(II)	10	0.67	2.91	0.60	0.19	0.54	0.08
Co(II)	10	0.66	2.71	0.60	0.23	0.54	0.30
Zn(II)	10	0.66	1.69	0.60	0.29	0.54	0.15
Ni(II)	10	0.66	0.77	0.60	0.35	0.54	0.12

The consistency of calculated results when the analysis is performed by different users, on the same instrument, on different days was checked by running the intermediate precision test. Two different analysts have analyzed freshly prepared standard solutions for 10 days in a row. The corresponding % RSD values vary within the 0.11 – 0.51 % range (Table 7), fulfilling the % RSD < 0.60 % condition calculated with modified Horwitz equation, RSD $< 0.6\times 2^{(1-0.5\lg c)}$.

Table 7.

Method intermediate precision

	Analyte concentration [µg/L]	Analyst 1	Analyst 2	Horwitz equation modified
		RSD [%]	RSD [%]	
Pb(II)	100	0.51	0.41	0.59
Cu(II)	100	0.19	0.11	0.59
Cd(II)	100	0.19	0.21	0.60
Co(II)	100	0.23	0.20	0.60
Zn(II)	100	0.29	0.23	0.60
Ni(II)	100	0.35	0.20	0.60

The recovery tests were performed on deionised water samples spiked with increasing amounts of all six metals standard solutions. Samples collected in Bucharest, next to the North Railway Station, Rahova, and Drumul Taberei districts, as well as downtown, on the Icechim site were also spiked with the increasing amounts of standard calibration solution and analyzed. The recovery degree (%) of samples fortified with analytes was evaluated as the difference between the spiked and unspiked sample concentration against the spiking analyte concentration. The calculated recovery varies within the 95 – 107 % range, as shown by data collected in Table 8.

Uncertainty evaluation represents part of the validation plan for many '*in–house*' developed analysis methods. Fig. 3 presents the sources of uncertainty taken into account while establishing the uncertainties budget. Standard uncertainty values were obtained from calibration certificates and method repeatability, while the combined uncertainty was calculated according to the Gauss propagation rules.

Three different concentration levels (lowest concentration level of the calibration interval, c_1, median level, c_2, and upper concentration level of the calibration interval, c_3, for each analyte) were considered for the calculation of the expanded uncertainty. The cover factor used is 2, as the normal distribution of errors and 95 % confidence level conditions were considered. Calculated values are presented in Table 9, data demonstrating that the expanded standard uncertainty values are higher at lower concentrations and decrease as concentration increases.

The measurement uncertainty requires re-evaluation when one of the determining factors (personal, calibration equipment, environmental conditions, etc.) is changed or the legal or customer requirements for method performance are different. As shown in Fig. 3, the highest contribution to the expanded uncertainty comes from repeatability, which varies between 1.6 and 2.2% and from calibration curves, which vary between 1.3 and 1.6%. All other contributions considered for dilution operations when preparing the standards are lower than 0.9%, so future re–evaluation of uncertainty should concentrate on establishing the effect of changes upon the method repeatability.

Table 8.

Method recovery

Sample	Pb(II)		Cu(II)		Cd(II)		Co(II)		Zn(II)		Ni(II)	
	c_{cal} [µg/L]	Rec. [%]	c_{cal} [µg/L]	Rec. [%]	c_{cal} [µg/L]	Rec. [%]	c_{cal} [µg/L]	Rec. [%]	c_{cal} [µg/L]	Rec. [%]	c_{cal} [µg/L]	Rec. [%]
DW	-	-	-	-	-	-	-	-	-	-	-	-
DW+100 µg/L	99.61	-	103.32	-	103.39	-	103.36	-	103.39	-	98.56	-
DW+200 µg/L	200.06	-	205.23	-	205.40	-	205.26	-	205.40	-	209.64	-
M_I	10.56	-	7.23	-	178.45	-	-	-	4.21	-	-	-
M_I + 100 µg/L	110.19	100.02	106.46	96.04	283.54	101.64	102.89	99.54	103.54	96.07	95.36	96.75
M_I + 200 µg/L	207.28	98.33	209.22	98.42	406.34	110.95	205.70	100.21	206.34	98.41	210.66	100.48
M_{GN}	5.17	-	4.15	-	344.89	-	-	-	18.31	-	-	-
M_{GN}+100 µg/L	106.10	101.32	107.91	100.42	447.16	98.91	103.19	99.83	124.16	102.80	103.85	105.39
M_{GN}+200 µg/L	200.99	97.88	199.77	95.28	560.79	105.11	205.87	100.29	226.79	101.50	210.48	100.40
M_R	4.58	-	3.86	-	46.85	-	-	-	21.54	-	-	-
M_R +100 µg/L	100.63	96.42	104.91	97.80	152.05	101.75	103.39	100.03	124.48	99.56	103.93	105.45
M_R +200 µg/L	200.98	98.17	206.61	98.76	260.86	104.19	205.68	100.20	226.86	99.96	210.42	99.88
M_{DR}	4.98	-	5.32	-	65.61	-	-	-	87.15	-	-	-
M_D +100 µg/L	111.56	106.99	119.24	110.26	164.26	95.41	103.42	100.06	194.26	103.60	103.79	105.30
M_{DR}+200 µg/L	201.97	98.71	211.46	100.44	268.72	98.88	205.81	100.27	296.72	102.03	210.41	99.88

DW = deionized water; M_{GN} = North Railway Station, M_R= Rahova district; M_I = Icechim, M_{DR} = Drumul Taberei district

Table 9.

Method uncertainty

	c_1	$U_{exp.}$	c_2	$U_{exp.}$	c_3	$U_{exp.}$
	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]	[µg/L]
Pb(II)	50	2.16	100	1.34	200	0.73
Cu(II)	50	2.25	100	1.31	200	0.69
Cd(II)	50	2.10	100	1.29	200	0.84
Co(II)	50	2.14	100	1.41	200	0.73
Zn(II)	50	2.09	100	1.25	200	0.81
Ni(II)	50	2.27	100	1.39	200	0.76

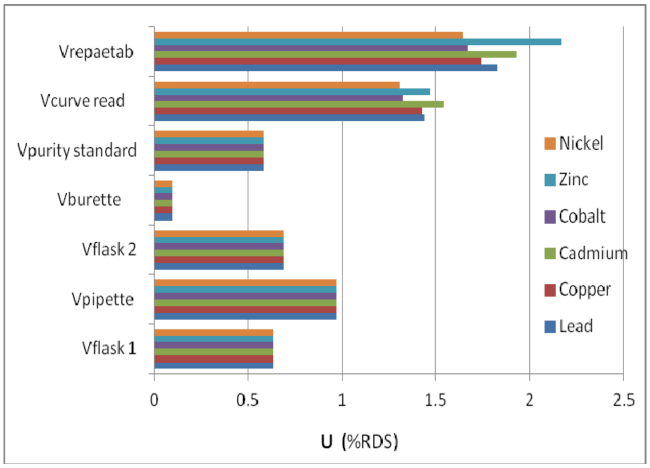

Fig. 3. Standard uncertainties

Real samples collected from west side of Bucharest urban area in December 2012 – March 2013 were analyzed for lead, copper, cadmium, cobalt, zinc, and nickel content using the *in–house* validated method. The concentration follows the Cd^{2+}> Zn^{2+-} > Pb^{2+}> Cu^{2+} pattern. Nickel and cobalt were not detected. Results in Table 10 signal a higher cadmium level in the Pacii district, 671.15 µg/L. The North Railway Station displays half the level, 344.88 µg/L and Icechim downtown has four times less, namely 178.4 µg/L. The other samples contained eight times less cadmium. The zinc content varies within the 4.2 – 90.0 µg/L range. As for lead and copper, their concentrations are approximately equal, with values ranging between 4.5 and 10.5 µg/L for lead, and 3.8 – 7.3 µg/L for copper. In case of copper and zinc, the official limit values are not exceeded, for lead only 10% of the samples exceed the limit and for cadmium over 50% of the samples outweigh by far the allowed value according the law 311/2004 for drinking water.

Table 10.

Transition metals levels in Bucharest urban areas

Sample	Pb(II) [µg/L]	Cu(II) [µg/L]	Cd(II) [µg/L]	Zn(II) [µg/L]
M_I	10.56±2.3	7.23±2.2	178.4±5.1	4.21±1.6
M_R	4.58±0.1	3.86±0.1	46.85±4.4	21.54±0.8
M_{GN}	5.17±0.3	4.15±0.1	344.88±4.6	18.31±0.7
M_{DR}	4.98±0.6	5.32±0.1	65.61±1.6	87.15±1.1
M_P	4.45±0.1	3.88±0.1	671.15±2.9	15.60±0.4
M_C	4.73±0.4	3.89±0.1	52.97±1.2	54.89±0.8

DW = deionized water; M_{GN} = North Railway Station, M_R= Rahova district;
M_I = Icechim, M_{DR} = Drumul Taberei district M_P = Pacii district; M_C = CET South

4. Conclusions

Lead, copper, cadmium, cobalt, zinc, and nickel were simultaneously determined from wet depositions using an automated ion chromatograph ICS3000 Dionex system equipped with an isocratic eluent delivery pump, isocratic derivatisation reagent pump, CS5 separation column, WTV molecular absorption detector, and an AS40 autosampler. The method was subjected to '*in–house*' validation, before shifting to routine exploitation. Since the relative standard deviation of retention times was smaller than 1 % and the peaks resolution exceeded the 1.5 min condition, method was declared selective. Linear calibration curves were obtained in the 50–500 µg/L concentration range, characterized by slopes between 0.03 and 0.30 with standard deviations, s_b, of 0.01 – 0.15, intercepts between 0.1 and 9.0 and intercepts standard deviations s_a, between 4.0 and 32, and correlation coefficients of 0.999.

The relative standard deviation values of the peak areas determined in conditions of intermediate precision were slightly smaller than those determined in conditions of repeatability, proving that there are no other sources of error (analyst, solution preparation or environmental conditions). The calculated %RSD values vary below the maximum allowed 9.6 % limit. The validation of the proposed analytical method has been successfully performed and it was further used to analyze the cantion content in wet depositions collected from several urban and industrial areas in Bucharest. The major metals found were lead, copper, cadmium, and zinc, the concentration pattern being $Cd^{2+} > Zn^{2+-} > Pb^{2+} > Cu^{2+}$.

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REFERENCES

[1] *Arsenea, C., Olariua, R. I., Mihalopoulos, N.* Chemical composition of rainwater in the northeastern Romania, Iasi region (2003–2006), Atmospheric Environment **41**, 2007, pp. 9452–9467.

[2] *Bertrand, G., Celle-Jeanton, H., Laj, P., Rangognio, J., & Chazot, G.*, Rainfall chemistry: long range transport versus below cloud scavenging. A two-year study at an inland station (Opme France), Journal of Atmospheric Chemistry **60**, 2008, pp. 253-271. DOI 10.1007/s10874-009-9120-y.

[3] *Bridges, K. S., Jickells, T. D., Davies, T. D., Zeman, Z., & Hunova, I.,* Aerosol, precipitation and cloud water chemistry observations on the Czech Krusne Hory plateau adjacent to a heavily industrialized valley. Atmospheric Environment **36**, 2002, pp. 353–360. DOI: 10.1016/S1352-2310(01)00388-0.

[4] *Bytnerowicz, A., Badea, O., Popescu, F., Musselman, R., Tanase, M., Barbu, I., Fraczek, W., Gembasu, N., Surdu, A.,Danescu, F., Postelnicu, D., Cenusa, R., Vasile, C.*, Air pollution, precipitation chemistry and forest health in the Retezat Mountains, southern Carpathians, Romania, Environmental Pollution **137**, 2005, pp. 546–567. DOI 10.1016/j.envpol.2005.01.040.

[5] *Han, G., Wu, Q., & Tang, Y.,* Acid rain and alkalization in south-western China: chemical and strontium isotope evidence in rainwater from Guiyang, Journal of Atmospheric Chemistry **68**, 2012, pp. *139*-155. DOI 10.1007/s10874-012-9213-x

[6] *Hlawiczka, S., Dyduch, B., & Fudala, J.*, Long-term changes of particulate emission in the industrial region of upper Silesia (Poland) and their effect on the acidity of rainwater, Water, Air, and Soil Pollution **142**, 2003, pp. 151–163.

[7] *Josceanu, A. M., Postelnicescu, P., & Dumitrescu, A. M.,* Validation of an ion chromatographic method for lead and cooper quantification. In Proceedings of the 37th International Conference of Slovak Society of Chemical Engineering, May 24–28, 2010 (Po-Tu-4, 296p.pdf, pp. 471–476). Tatranské Matliare: Slovak Society of Chemical Engineering.

[8] *Lopez-Moreno, C., Viera, I., & Urbano, A. M.,* Validation of an ion chromatographic method for the quantification of anions in water, Desalination **261**, 2010, pp. 111-116. DOI: 10.1016/j.desal.2010.05.022.