Validation of an Ion Chromatographic Method for Determination of Anions in Wet Depositions

IRINA BAJENARU (CIOBANU)[1]*, IULIAN MINCA[1], CORNELIA GURAN[1], ANA MARIA JOSCEANU[2], FANICA BACALUM[3]

[1] University Politehnica of Bucharest, Department of Applied Physical Chemistry, Inorganic Chemistry and Electrochemistry, 1-5 Polizu Str., 011061, Bucharest, Romania

[2] University Politehnica of Bucharest, Department of Analytical Chemistry and Environmental Engineering, 1-5 Polizu Str., 011061, Bucharest, Romania

[3] National Research& Development Institute for Chemistry and Petrochemistry ICECHIM, 202 Splaiul Independentei, 060041, Bucharest, Romania

This project validates an ion chromatographic procedure for the simultaneous determination of F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} ions in wet depositions and other meteoric water sources. An ICS3000 Dionex system equipped with conductivity detector was employed in evaluating the method performances. The proposed method proves to be selective, and calibration curves are linear in the 0.04 – 0.2 mg/L concentration range of F^-, 0.2 - 5 mg/L concentration range of Cl^-, NO_3^-, Br^- and SO_4^{2-}, and 0.4 – 10 mg/L concentration range of PO_4^{3-}, characterized by slopes of 0.06 - 0.40, with standard deviations, s_b, of 0.02 – 0.23, intercepts of 0.00, with standard deviations, s_a, between 0.07 and 0.22, and correlation coefficients of 0.995 for each ion of interest. The calculated limits of detection (LOD) and limits of quantification (LOQ) for independent fortified samples were in the 0.001 - 0.02 mg/L and 0.004 – 0.06 mg/L range respectively. Repeatability and intermediate precision tests gave RDS% between 0.65 and 2.19 %, 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 atmospheric pollution.

Keywords: method validation, meteoric waters, IC

Since the last decades, the chemical composition of precipitations is strongly investigated in many areas of the world. The studies were focused on the chemical interactions, the distribution of precipitation, the sources of components in wet depositions (marine source, terrestrial source, and anthropogenic source) and meteorological variation (Guilin Han et al., 2012; Bertrand et al.).

There are few studies concerning the chemical composition of wet depositions compositions for Eastern Europe, mainly in Poland and Czech republic (Polkowska et al., 2005; Hunova et al., 2004; Hlawiczka et al., 2003; Bridges et al., 2002). For Romania there are two reports on the chemical composition of rainwater in a mountain area (Bytnerowicz et al., 2005) and Iasi city (Arsene et al., 2007).

Ion chromatographic monitoring of aqueous samples represents a fast, small volume sample demand and reliable method for determination of anions and cations, as many international applied standards demonstrate. 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 procedures towards routine exploitation (Josceanu et al., 2010; Lopez et al., 2010). The aim of this project is validation of an ion chromatographic procedure for the simultaneous determination of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate ions in wet depositions and other meteoric water sources. An ICS3000 Dionex system equipped with conductivity detector for anion analysis was employed in evaluating the method linearity, repeatability, intermediate precision, accuracy, selectivity, limits of detection and quantification.

Experimental part

The seven anions set (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) was analysed by using an ICS 3000 Dionex ion chromatographic system (Thermo Scientific) composed of an isocratic pump, Ion Pac AS22 separation column, Ion Pac AG22 guard column, ASRS 300 suppressor and conductivity detector.

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 an Easy Pure Rodi (Branstead) system was used for preparing solutions.

Snow samples were collected from six points in Bucharest (fig.1), using a homemade polyethylene sampler, further treated with HNO_3, 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.

Certified 20 mg/L F^-, 100 mg/L Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-} and 200 mg/L PO_4^{3-} Combined Seven Anion Standard for ion chromatography, traceable to SRM NIST, were purchased from Dionex. All calibration solutions were prepared by appropriate dilution. 0.45μm pore diameter membrane syringe filters were used for sample particulate removal. The volumetric glassware used for standard solutions preparation was class A.

The mobile phase was prepared by diluting 1:100 an eluent concentrate solution from Dionex, containing 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ with deionised water. All chromatographic experiments were carried out in the isocratic mode, at 30°C. The operating conditions were: 1 mL/min eluent flow rate, 1000 μL injection volume and 25μL injection loop volume, 26 mA current in suppressor.

Data processing was carried out with Excel.

* email: bajenarugentiana@yahoo.com; Tel.: 0727822505

Fig. 1 Snow collection points (M_P = Pacii district; M_{DR} = Drumul Taberei district; M_R = Rahova district; M_I = Icechim; M_{GN} = North Railway Station; M_C = CET South)

Results and discussions

The seven anions are separated by a CO_3^{2-} / HCO_3^- eluent according to the sequence presented in the chromatogram recorded at a 0.4 mg/L F^-, 2 mg/L Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-} and 4 mg/L PO_4^{3-} concentration level (fig. 2).

Selectivity/ Specificity

The selectivity was evaluated by examining the relative standard deviation (% RSD) of the retention times for a 24 injections set at eight different concentration levels, the concentration of ions varying as follows: 0.04 – 0.2 mg/L concentration range for F^-, 0.2 - 5 mg/L concentration range for Cl^-, NO_2^-, Br^- and SO_4^{2-}, and 0.4 – 10 mg/L concentration range for PO_4^{3-}. The average retention times and relative standard deviations are collected in table 1. As in all cases the relative standard deviation is less than 1 %, the method is declared selective.

Linearity

Calibration curves were obtained in the 0.04–2 mg/L concentration range for F^-, 0.2-5 mg/L for Cl^-, NO_2^-, Br^-, NO_3^-, and SO_4^{2-}, and 0.4 - 10 mg/L PO_4^{3+} (figs. 3-9). Experiments run at eight concentration levels, using three replicate injections for each concentration level of anion gave linear fit for all ions in terms of peak area, characterized by slopes between 0.06 and 0.40 with standard deviations, s_b, of 0.02 – 0.23, intercepts of 0.00, and intercepts standard deviations s_a, between 0.07 and 0.22 (table 2). Examination of standard residuals demonstrated the lack of outliers for all seven calibration curves.

Accuracy

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 3

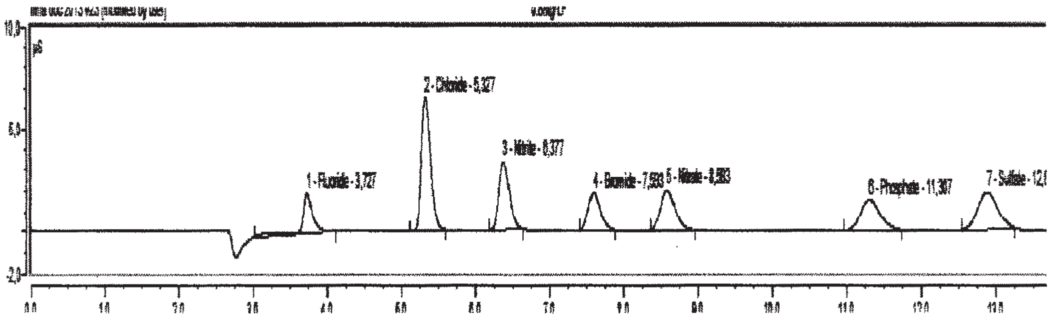

Fig. 2. Typical chromatogram for a standard solution (0.4 mg/L F^-, 2 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 4 mg/L PO_4^{3-}) recorded with an ICS 3000 equipment for 1.00 mL/min eluent flow rate, at 30 °C

Table 1
METHOD SELECTIVITY (%RSD)

Analyte	Retention time (min)	*s* (min)	RSD (%)
F^-	3.73	0.02	0.47
Cl^-	5.32	0.01	0.28
NO_2^-	6.38	0.02	0.35
Br^-	7.59	0.03	0.36
NO_3^-	8.59	0.03	0.40
PO_4^{3-}	11.31	0.06	0.50
SO_4^{2-}	12.87	0.06	0.50

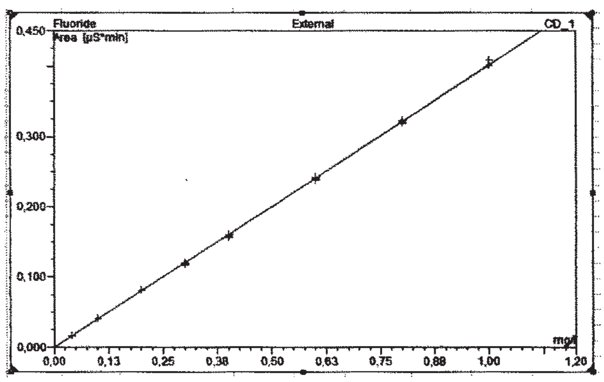

Fig. 3 Calibration curve for F^- (0.04 – 2 mg/L)

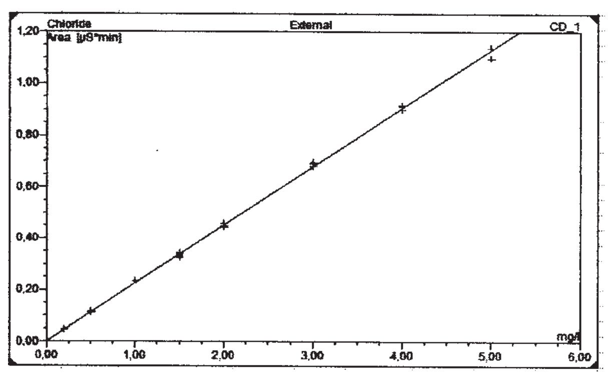

Fig. 4 Calibration curve for Cl^- (0.2-5 mg/L)

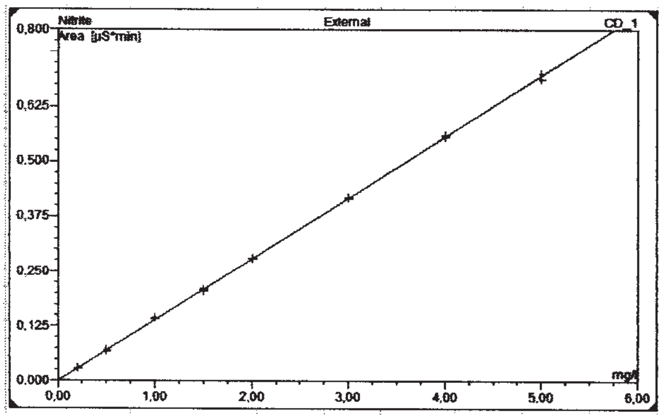

Fig. 5 Calibration curve NO_2^- (0.2-5 mg/L)

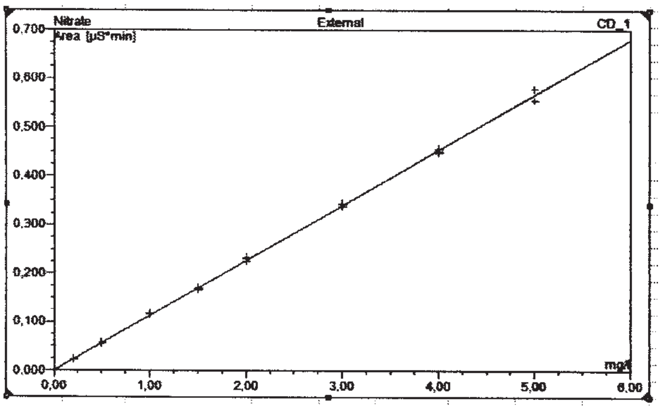

Fig. 7 Calibration curve for NO_3^- (0.2-5 mg/L)

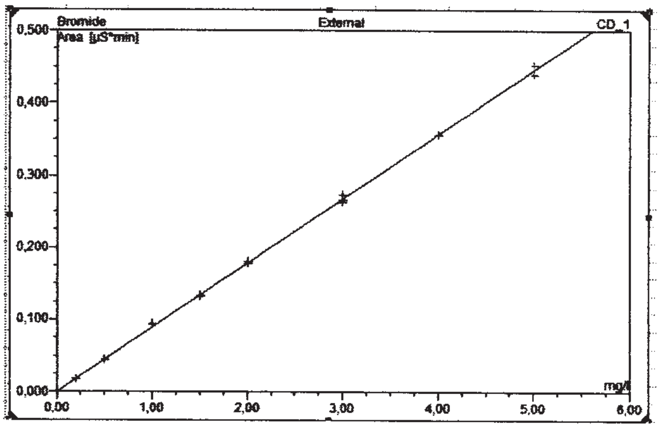

Fig. 6 Calibration curve for Br^- (0.2-5 mg/L)

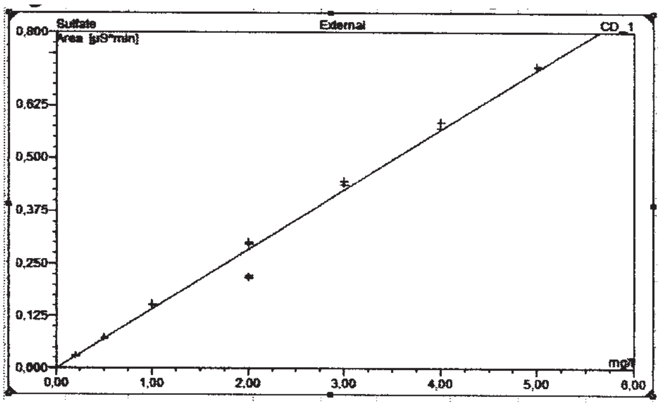

Fig. 8 Calibration curve for SO_4^{2-} (0.2-5 mg/L)

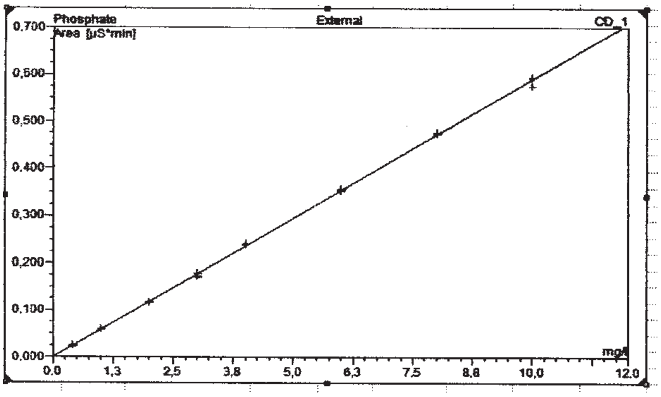

Fig. 9 Calibration curve for PO_4^{3-} (0.4-10 mg/L)

Table 2
REGRESSION ANALYSIS RESULTS FOR THE CALIBRATION CURVES

Anion	Slope (b)	Slope standard deviation, (s_b)	Intercept (a)	Intercept standard deviation (s_a)	Correlation coefficient (R^2)	Response standard deviation (s_y)
F^-	0.40	0.23	0.00	0.12	0.999	0.21
Cl^-	0.22	0.08	0.00	0.22	0.999	0.37
NO_2^-	0.14	0.05	0.00	0.12	0.999	0.21
Br^-	0.09	0.02	0.00	0.07	0.999	0.11
NO_3^-	0.11	0.04	0.00	0.12	0.999	0.20
PO_4^{3-}	0.06	0.02	0.00	0.11	0.999	0.19
SO_4^{2-}	0.14	0.05	0.00	0.13	0.995	0.002

Anion	Level 1[a]	Level 2[b]	Level 3[c]	Level 4[d]	Level 5[e]	Level 6[f]	Level 7[g]	Level 8[h]
F^-	2.73	2.21	1.98	0.64	-0.41	-0.44	0.10	0.35
Cl^-	2.09	-0.03	3.74	-0.99	-0.71	1.53	0.42	-1.11
NO_2^-	1.49	-0.13	3.14	-0.54	0.37	0.12	0.07	-0.32
Br^-	1.73	-0.39	4.36	-0.68	0.41	0.06	-0.40	0.12
NO_3^-	1.82	-0.85	2.89	-0.97	1.52	0.60	-0.59	-0.11
PO_4^{3-}	1.19	0.11	-1.70	0.91	1.60	0.18	0.80	-0.99
SO_4^{2-}	3.79	1.02	7.42	2.23	5.35	3.99	2.39	1.25

[a]0.04 mg/L F^-, 0.2 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 0.4 mg/L PO_4^{3-};
[b]0.1 mg/L F^-, 0.5 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 1 mg/L PO_4^{3-};
[c]0.2 mg/L F^-, 1 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 2 mg/L PO_4^{3-};
[d]0.3 mg/L F^-, 1.5 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 3 mg/L PO_4^{3-};
[e]0.4 mg/L F^-, 2 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 4 mg/L PO_4^{3-};
[f]0.6 mg/L F^-, 3 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 6 mg/L PO_4^{3-};
[g]0.8 mg/L F^-, 4 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-} and 8 mg/L PO_4^{3-};
[h]1 mg/L F^-, 5 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 10 mg/L PO_4^{3-}.

Table 3
METHOD ACCURACY

	LOD [mg/L]			LOQ [mg/L]		
	Lower concentration	Calibration data (intercept)	Calibration data (line)	Lower concentration	Calibration data (intercept)	Calibration data (line)
F^-	0.001	2.27	1.74	0.004	6.89	5.26
Cl^-	0.01	3.19	5.37	0.04	9.67	16.27
NO_2^-	0.006	2.91	4.90	0.02	8.81	14.85
Br^-	0.006	2.43	4.09	0.02	7.36	12.40
NO_3^-	0.006	3.52	5.94	0.02	10.68	17.99
PO_4^{3-}	0.017	6.43	10.84	0.06	19.47	32.86
SO_4^{2-}	0.008	3.02	5.06	0.03	9.16	15.36

Table 4
METHOD DETECTION LIMIT AND QUANTIFICATION LIMITs

replicates. They were performed on deionised water samples spiked with increasing levels of anions standard solution. The bias values in table 3 vary within the -0.99 - 5.33 % range.

Limit of detection (LOD) and limit of quantification (LOQ)

The detection and quantification limits were obtained from the calibration curves, by multiplying the standard deviation of the lower concentration by 3 and 10 respectively or by multiplying the residual standard deviation or the standard deviation of the intercept by 3.3 and 10 respectively.

Results collected in table 4 show different values, depending on the calculation strategy. Detection and quantification limits, from the lowest detectable concentration provide the lowest LOD values for all seven anions: 0.001 – 0.02 mg/L, while LOQ were within the 0.004 – 0.06 mg/L range. Limits obtained from the standard deviation of the calibration curve ($s_{y/x}$) are larger than those obtained from the other approaches, except for F^-. LOD and LOQ values estimated from standard deviation of intercepts (s_a) vary between 2.27 and 6.45 mg/L for LOD, and 6.90 – 19.5 mg/L for LOQ. 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.

Repeatability

The repeatability test checks the consistency of calculated results for the analyte peak over a short time period, by the same user, on the same instrument. As shown in table 5, the relative standard deviations of the peak areas vary between 0.65 and 2.20, all fulfilling the requirements derived from the Horwitz equation at the employed concentration levels.

Anion	No. of replicates	Low concentration*		Medium concentration**	
		s [mg/L]	RSD [%]	s [mg/L]	RSD [%]
F^-	10	0.0004	0.97	0.006	1.55
Cl^-	10	0.004	2.19	0.015	0.74
NO_2^-	10	0.002	1.11	0.02	0.93
Br^-	10	0.002	1.05	0.01	0.67
NO_3^-	10	0.002	0.98	0.002	2.14
PO_4^{3-}	10	0.006	1.42	0.03	0.64
SO_4^{2-}	10	0.003	1.39	0.03	1.77

* 0.04 mg/L F^-, 0.2 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 0.4 mg/L PO_4^{3-};
** 0.4 mg/L F^-, 2 mg/L Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, and 4 mg/L PO_4^{3-}.

Table 5
METHOD REPEATABILITY

	Analyte concentration [mg/L]	Analyst 1		Analyst 2	
		s [mg/L]	RSD [%]	*s* [mg/L]	RSD [%]
F^-	0.1	0.001	0.76	0.001	0.63
Cl^-	0.5	0.004	0.80	0.003	0.63
NO_2^-	0.5	0.003	0.54	0.004	0.71
Br^-	0.5	0.006	1.15	0.003	0.59
NO_3^-	0.5	0.003	0.51	0.004	0.71
PO_4^{3-}	1.0	0.009	0.89	0.015	1.46
SO_4^{2-}	0.5	0.004	0.88	0.002	0.45

Table 6
METHOD INTERMEDIATE PRECISION

Intermediate precision

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 0.50 - 1.46 % range (table 6), fulfilling the % RSD < 2 % condition.

Control diagrams for each anions of interest were also designed. Figures 10-16 signal the presence of few consecutive values with an increasing or decreasing tendency, as well as values located on the same side of centre line (X_m). There were no values below the inferior control limit (LCI) or the superior control limit (LCS).

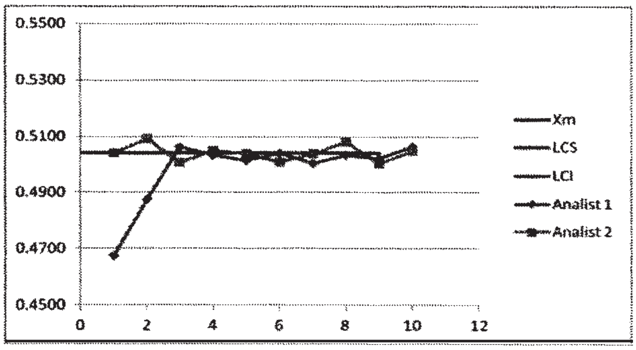

Fig. 13 Intermediate precision diagram for Br^-

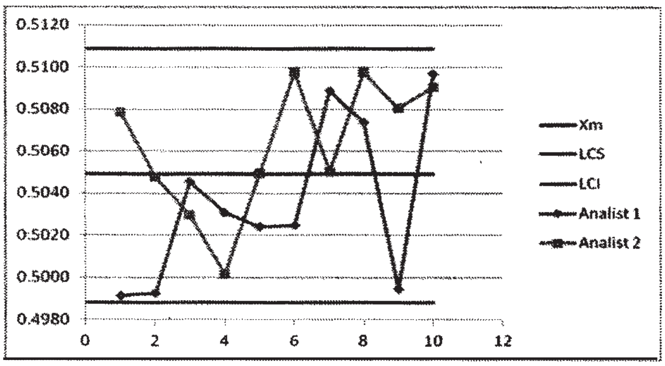

Fig. 10 Intermediate precision diagram for F^-

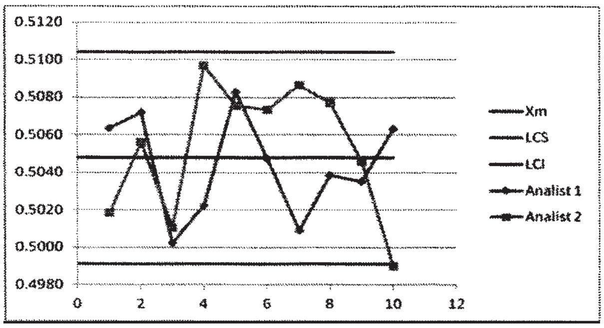

Fig. 14 Intermediate precision diagram for NO_3^-

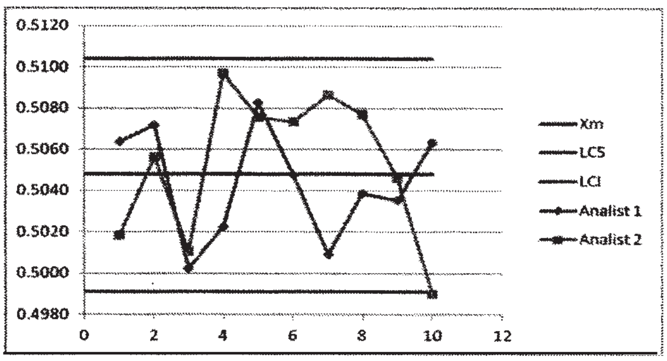

Fig. 11 Intermediate precision diagram for Cl^-

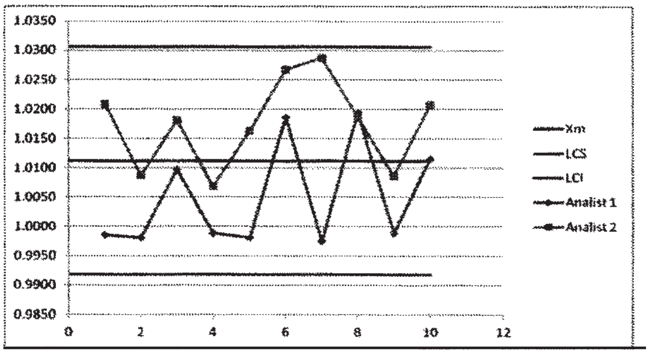

Fig. 15 Intermediate precision diagram for PO_4^{3-}

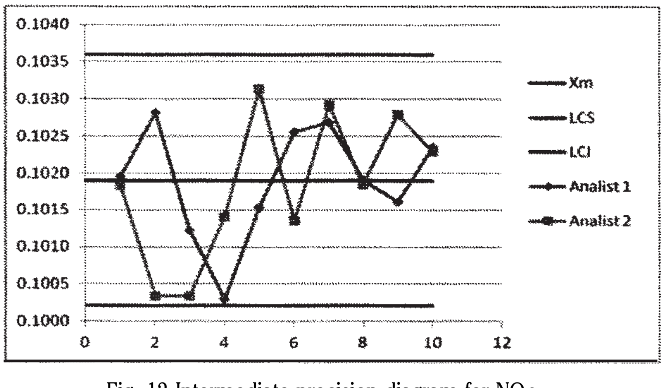

Fig. 12 Intermediate precision diagram for NO_2^-

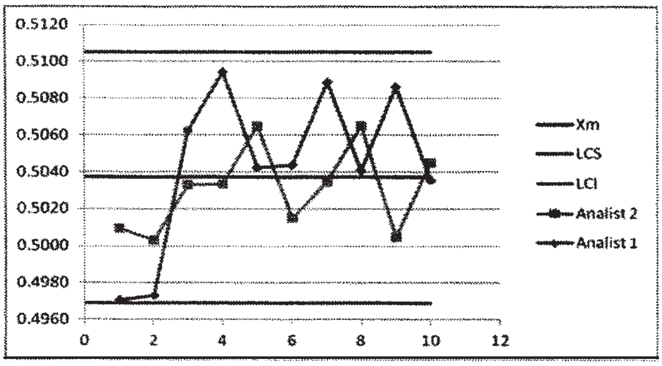

Fig. 16 Intermediate precision diagram for SO_4^{2-}

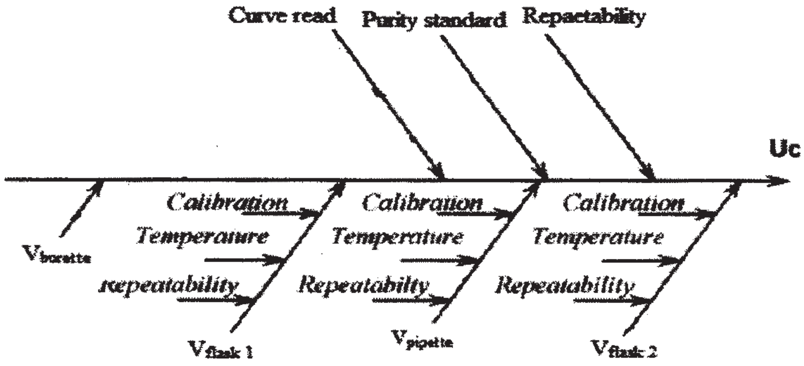

Fig. 17. Uncertainty sources in the determination of F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-}

Table 7
METHOD RECOVERY

Sample	F^-		Cl^-		NO_2^-		Br^-		NO_3^-		PO_4^{3-}		SO_4^{2-}	
	c_{cal} [mg/L]	Rec. [%]	c_{cal} [mg/L]	Rec. [%]	c_{cal} [mg/L]	Rec. [%]	c_{cal} [mg/L]	Rec. [%]	c_{cal} [mg/L]	Rec. [%]	c_{cal} [mg/L]	Rec. [%]	c_{cal} [mg/L]	Rec. [%]
DW	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DW +3 mg/L	0.61	-	3.32	-	3.39	-	3.36	-	3.39	-	5.86	-	3.33	
DW+5 mg/L	1.06	-	5.23	-	5.40	-	5.26	-	5.40	-	9.64	-	5.39	
M_I	0.97	-	3.65	-	-	-	-	-	0.60	-	-	-	0.58	-
M_I + 3 mg/L	1.64	109.05	6.46	84.86	3.54	104.24	2.89	85.89	3.54	86.66	5.36	91.57	3.70	93.73
M_I + 5 g/L	1.91	88.80	9.22	106.63	6.34	117.4	5.70	108.33	6.34	106.40	10.66	110.54	6.66	112.77
M_{GN}	0.1	-	4.10	-	-	-	-	-	0.78	-	-	-	0.81	-
M_{GN} + 3 mg/L	0.61	82.88	7.91	114.58	4.16	102.67	3.19	95.01	4.16	99.55	5.85	99.93	4.43	108.73
M_{GN} + 5 mg/L	0.99	84.66	9.77	108.31	6.79	105.77	5.87	102.99	6.79	111.24	10.48	108.72	6.94	113.67
M_R	0.13	-	1.09	-	-	-	-	-	0.92	-	-	-	1.08	-
M_R + 3 mg/L	0.63	81.87	4.91	115.05	4.05	119.49	3.39	100.94	4.48	104.91	5.93	96.73	4.72	109.12
M_R + 5 mg/L	0.98	79.93	6.61	105.60	6.86	127.05	5.68	107.96	6.86	110.01	10.42	105.29	7.13	112.26
M_{DR}	0.95	-	15.85	-	-	-	-	-	0.85	-	-	-	0.80	
M_{DR} + 3 mg/L	1.56	100.55	19.24	102.18	4.26	105.49	3.42	101.84	4.26	100.32	5.79	98.89	4.28	104.32
M_{DR} + 5 mg/L	1.97	96.71	21.42	106.59	6.72	106.05	5.81	110.48	6.72	108.74	10.41	107.97	6.78	110.84

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

Recovery

The recovery tests were performed on deionised water samples spiked with increasing amounts of all seven anions standard solutions. Samples collected in Bucharest, next to the North Railway Station, Rahova, and Drumul Taberei districts, as well as downtown, at Icechim were also spiked with the increasing amounts of standard calibration solution and analyzed. The recovery (%) 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 84 - 118 % range, as shown by data collected in table 7.

Uncertainty evaluation

Uncertainty evaluation represents part of the validation plan for many '*in-house*' developed analysis methods. Figure 17 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 8, data demonstrating that the expanded standard uncertainty values are higher at lower concentrations and decrease as concentration increases. Determination of chloride at 0.2 mg/L is

Table 8
METHOD UNCERTAINTY

	c_1 [mg/L]	$U_{exp.}$ [mg/L]	c_2 [mg/L]	$U_{exp.}$ [mg/L]	c_3 [mg/L]	$U_{exp.}$ [mg/L]
F^-	0.04	0.02	0.4	0.03	1	0.01
Cl^-	0.2	0.04	2	0.01	5	0.01
NO_2^-	0.2	0.02	2	0.02	5	0.004
Br^-	0.2	0.02	2	0.01	5	0.003
NO_3^-	0.2	0.02	2	0.02	5	0.01
PO_4^{3-}	0.4	0.03	4	0.01	10	0.007
SO_4^{2-}	0.2	0.03	2	0.03	5	0.01

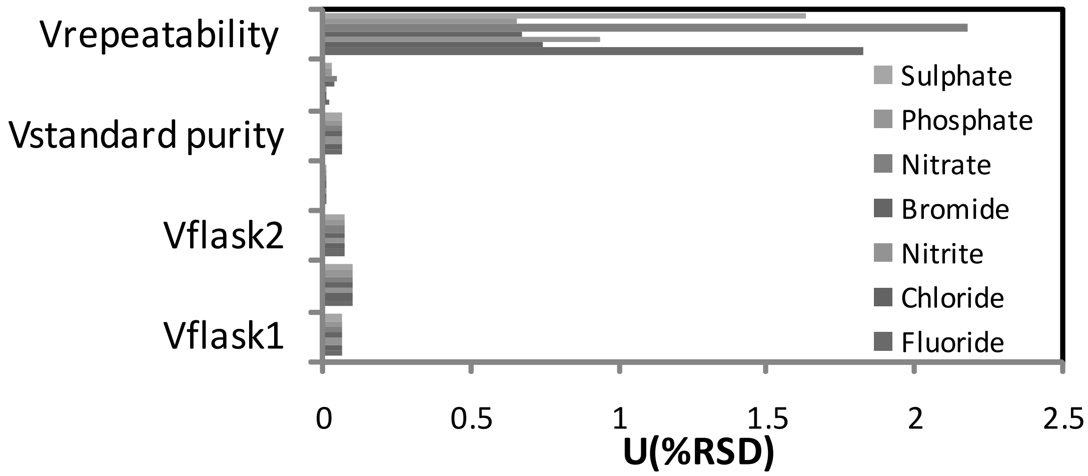

Fig. 18. Standard uncertainties in the calculated values

Table 9
ANIONS LEVELS IN BUCHAREST URBAN AREAS

Sample	N	F^- [mg/L]	Cl^- [mg/L]	NO_3^- [mg/L]	SO_4^{2-} [mg/L]
DW	4	-	-	-	-
M_I	4	0.97 ±0.04	3.65±0.06	0.60±0.01	0.58 ±0.01
M_R	4	0.14±0.01	1.09±0.04	0.92±0.02	1.08±0.02
M_{GN}	4	0.10±0.03	4.10±0.06	0.78±0.01	0.81±0.01
M_{DR}	4	0.95±0.08	15.9±0.02	0.85±0.01	0.80±0.01
M_P	4	0.08±0.01	1.79±0.03	0.77±0.02	0.23±0.01
M_C	4	0.03±0.01	0.99±0.05	0.75±0.01	0.29±0.01

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

associated with the highest evaluated expanded uncertainty, 0.04 mg/L.

The measurement uncertainty requires re-evaluation when one of the determining factors (personal, calibration equipment, environmental conditions, etc.) is changed or the legal requirements or customer method performance. As shown in Figure 18, the highest contribution to expanded uncertainty comes from repeatability, which varies between 0.7 and 1.9%. All other contributions are lower than 0.5%, so future re-evaluation of uncertainty should concentrate on establishing the effect of changes upon the method repeatability.

Evaluation of anions content in urban areas

Real samples collected from west side of Bucharest urban area in December 2012 – March 2013 were analyzed for F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} content using the *in-house* validated method. Fluoride, chloride, nitrate, and sulphate were identified and quantified in all samples. The concentration follows the $Cl^- > SO_4^{2-} > NO_3^- > F^-$ pattern. Results in Table 9 signal a higher fluoride level in the Icechim downtown and Drumul Taberei district collection points, 0.95 and 0.95 mg/L. The other samples have eight times less fluoride. The chloride content varies within the 0.99 - 4.10 mg/L range. As for nitrate and sulphate, their concentrations are approximately equal, with values ranging between 0.6 and 0.92 mg/L for nitrate, and 0.6 – 1.1 mg/L for sulphate respectively. The snow in industrial area CET South contained medium levels of Cl^-, NO_3^- and SO_4^{2-}.

Conclusions

F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} were simultaneously determined from wet depositions using an automated ion chromatograph ICS3000 Dionex equipped with conductivity detector and using an isocratic eluent delivery mode. The method was subject 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 for 0.04-10 mg/L concentration range, characterized by slopes between 0.11 and 0.40, with standard deviations, s_b, of 0.02 – 0.23, intercepts of 0.00, with standard deviations, s_a, between 0.07 and 0.22 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 %. The validation of the proposed analytical method has been successfully performed and it was further used to analyze the anion content in wet depositions collected from several urban and industrial areas in Bucharest. The major anions found were F^-, Cl^-, NO_3^-, and SO_4^{2-}, the concentration pattern being $Cl^- > SO_4^{2-} > NO_3^- > F^-$.

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References

1. ARSENEA, C., OLARIUA,R. I., MIHALOPOULOS, N. Atmospheric Environment 41, 2007, p. 9452–9467.
2.BERTRAND, G., CELLE-JEANTON, H., LAJ, P., RANGOGNIO, J., % CHAZOT, G. Journal of Atmospheric Chemistry 60, 2008, p. 253-271. DOI 10.1007/s10874-009-9120-y.

3.BRIDGES, K.S., JICKELLS, T.D., DAVIES, T.D., ZEMAN, Z., & HUNOVA, I. Atmospheric Environment 36, 2002, p. 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. Environmental Pollution 137, 2005, p.546–567. DOI 10.1016/j.envpol.2005.01.040.
5.HAN, G., WU, Q., & TANG, Y. Journal of Atmospheric Chemistry 68, 2012, p. 139-155. DOI 10.1007/s10874-012-9213-x.
6.HLAWICZKA, S., DYDUCH, B., & FUDALA, J. WATER. Air, and Soil Pollution 142, 2003, p. 151–163.
7.HUNOVA, I., SANTROCH, J., & OSTATNICKA, J. Atmospheric Environment 38, 2004, p. 887–898. DOI: 10.1016/j.atmosenv.2003.10.032.
8.JOSCEANU, A. M., POSTELNICESCU, P., & DUMITRESCU, A. M. 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.
9.LOPEZ-MORENO, C., VIERA, I., & URBANO, A. M. Desalination 261, 2010, p. 111-116. DOI: 10.1016/j.desal.2010.05.022.
10.POLKOWSKA, Z., ASTEL, A., WALNA, B., MALEK, S., MEDRZYCKA, K., GORECKI, T., SIEPAK, J., & NAMIESNIK, J. Atmospheric Environment 39, 2005, p. 837–855. DOI:10.1016/jatmosenv.2007.08.046.

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