



Determination of Iodides from Groundwater and Surface Water using an Optimized Ion Chromatographic Method

VALERIU ROBERT BADESCU, OLGA TIRON, GABRIELA GEANINA VASILE*,
LAURENTIU RAZVAN DINU

National Research and Development Institute for Industrial Ecology ECOIND, 71-73 Drumul Podul Dambovitei Str., 060652, Bucharest, Romania

Abstract: *The research aimed to provide an optimized method for the determination of iodides concentration in groundwater and surface water sources using ion chromatography technique. The analyses were conducted by using a conductivity detector, with a 35 mM KOH mobile phase, at a flow rate of 1 mL/min, the temperature in the detector chamber and the intensity of the suppressor current being set at 35°C and 87 mA, respectively. The interferences given by other ions were also investigated, and the performance parameters were determined such as detection limit, quantification limit, accuracy, and recovery.*

Keywords: *iodides, ion chromatography, water sources*

1. Introduction

Iodine is an essential element required for the synthesis of thyroid hormones. Unfortunately, about two billion people are facing iodine deficiency, which is responsible for multiple disorders [1] causing serious health problems mainly at infants and young children with long-term consequences [2]. On the other hand, excess iodine content in the human diet can severely affect the hormone synthesis activity leading to goiter and hypothyroidism diseases [3, 4]. Besides that, research in the field underlined that providing iodine to the persons who have had a sufficient or excess concentration of this element increases the incidence of autoimmune diseases [5].

In water sources, iodine is predominantly found as iodide (I^-) or iodate (IO_3^-) [6]. Other forms in which iodine is present would be the periodate (IO_4^-), hypoiodite (IO^-), methyl iodide (CH_3I), ethyl iodide (C_2H_5I), propyl iodide (C_3H_7I), butyl iodide (C_4H_9I), and methylene iodide bromide (CH_2Br) [7].

It is worth to point out that organic and inorganic iodine species found in water sources can react with disinfection products and by-products (such as ozone, chlorine, and chloramine) found during potabilization flow, resulting iodinated disinfection by-products representing a potential carcinogenic source as they print genotoxic and cytotoxic properties to mammary cells [8].

The role of iodine in human health has outlined the need for the development of more sensitive analytical techniques for its investigation. Currently, advanced analytical techniques are used, methods' sensibility reaching ultra-trace level. Certain methods have become routine techniques for traceability in clinical or analytical laboratories. Other methods have been proposed for iodide and iodate anions analysis in aqueous solutions. such as catalytic methods (for 0.1 $\mu\text{g/L}$ detection limit) [9], ion-chromatographic (IC) methods in different variants (as for example IC and exchange capacity controllable columns and column-switching technique (for 5.7 $\mu\text{g/L}$ detection limit)) [10], IC coupled with an ultraviolet detector (for 9.45 nM detection limit) [11]. IC techniques are also used for the analysis of other inorganic ions (chloride, bromide, fluoride, etc.) [12-14].

Chromatographic methods are specially used for the determination of iodine species when coupled with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (for 0.010 $\mu\text{g/L}$ detection limit) [15]. An ICP-MS analysis technology for simultaneous determination of bromine and iodine in high-salinity water was also developed, a low detection limit of 0.015 $\mu\text{g/L}$ being obtained [16].

*email: gabriela.vasile@incdecoind.ro



In the literature, indirect iodine determination methods are also presented, for instance: atomic absorption methods, with a detection limit of 2.75 µg/L [17] or Inductively Coupled Plasma Atomic Emission Spectrometry Methods (ICP-EOS) (2 µg/L detection limit) [18].

Besides, chemical vapor generation, pneumatic nebulization, and ICP-EOS methods could be coupled to improve the sensibility of the analyses, obtained results indicating 0.02 µg/L detection limit for iodide determination, this technology is used mainly for investigations conducted on seawater and spring water sources [19].

The paper presents an ion-chromatographic technique for the analysis of iodide anions in surface water and groundwater sources. The study is addressing for the establishment of (1) the optimal parameters for element investigation by using ion-chromatograph coupled with a conductivity detector, (2) the performance parameters of the proposed method (detection and quantification limits, working range, linearity, precision, recovery) as well as covers (3) the validation tests for method's selectivity (interference tests).

2. Materials and methods

2.1. Reagents and materials

Anion separation column type AS20 4 x 250 mm; Preguard column type AG20 4 x 50 mm; Potassium hydroxide (KOH) pellets 85% (Scharlau); Certified Reference Material (CRM) Iodide standard for IC 1000 mg/L, Trace CERT; Potassium iodide puriss (KI) 99.88% (Sigma Aldrich); Ultrapure water type ASTM 1.

CRM 1000 mg/L Iodide, Trace CERT type, was used for the calibration curve, the following standard solutions being prepared: 2, 4, 6, 8, and 10 mg/L, respectively.

Results assessment was performed with potassium iodide reagent.

2.2. Equipment

Ion Chromatograph ICS-3000 (Dyonex, USA) with Dyonex AS-AP Autosampler.

Ultrapure water system ELX Technology Inside Milli-Q (Millipore).

2.3. Optimization tests of the operational parameters of the method

The selected operational column allows a good separation of the iodide anion, the retention time being about 11 minutes. For this reason and as also taking into consideration that studies reported at this stage were performed on synthetic solutions to avoid any possible interferences with other anions, the retention period was increased to 15 min.

Since the used detector was of the electrical conductivity type, the volume of the injection loop was chosen to be 250 µL that one may maximize signal strength from the detector.

To ensure optimal conditions for the calibration curve, a preliminary study was conducted for investigating the influence of the operational parameters on the detector's signal value.

Hence, the study required the testing of the various (1) eluent concentrations, the parameter being also known as the '*mobile phase*'. As long as the electrical conductivity depends on the temperature's value, the investigation of the (2) optimum temperature required in the detector and column compartments was also considered. (3) Mobile phase flow rate was another researched indicator. Electrochemical type of the suppressor required to set a (4) current intensity for which signal suppression is maximal. By electrochemical process, the anion suppressor provides H⁺ necessary to suppress HO⁻ ion, in this way ions resulting from water dissociation being combined, the process leading to a decrease of the electrical conductivity and background noise.

2.4. In-house validation experiments

The experimental tests required for *in-house* validation of the method involved the assessment of the following performance parameters: detection limit (LOD), quantification limit (LOQ), precision tests (reproducibility, intermediate precision), linearity (parameters of the calibration curve,

homogeneity of dispersions test), recovery. The details related to the conducted experimental analyzes are presented in Table 1.

Table 1. Experimental tests followed for *in-house* validation of the method.

LOD, LOQ	0.7 mg/L, 10 determinations
Calibration curve	2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, 10 mg/L
Homogeneity of dispersions test	2 mg/L and 10 mg/L, 10 determinations for each concentration
Reproducibility	6 mg/L, 9 determinations
Intermediate precision	6 mg/L, 18 analysis
Recovery	Drinking water enriched with 4 mg/L, 8 determinations

2.4. Interference studies

To identify the susceptible anions that could influence the results of determinations for the studied analyte, type of column, and implicitly the anions having affinity to this type and their abundance and frequency in the studied matrices (groundwater, surface water) were taken into consideration.

The selectivity of the proposed method was achieved by testing the interference given by fluoride, chloride, sulfate, thiocyanate, thiosulfate, and carbonate anions. For each anion, three concentrations were tested (for the same iodide concentration) and the recovery yield for iodide was calculating.

2.5. Real samples analyze

The research was conducted on 40 water samples (underground water, surface, spring, and geothermal water sources), each analysis being performed in duplicate.

3. Results and discussions

As it was mentioned above, for achieving a maximum intensity of the signal for iodide determination with IC method, optimization of the operational parameters which influence the signal's value is requiring, being tested: eluent concentration, the flow rate of the mobile phase, the temperature in the detector chamber, and intensity of the suppressor current.

3.1. Optimization of the eluent concentration (KOH)

Different values of eluent concentration (in a range of 3.5-50 mM KOH) were tested for 10 mg/L iodide concentration, obtained results being shown in Figure 1. As it could be noticed, the lowest concentration of the purifying phase conducting a low signal (0.55 μ S), a flattened shape of the peak being obtained (Figure 2). The highest signal of the conductivity detector was achieved at 35 mM KOH, in this case, the detector response being 3.42 μ S (Figure 3).

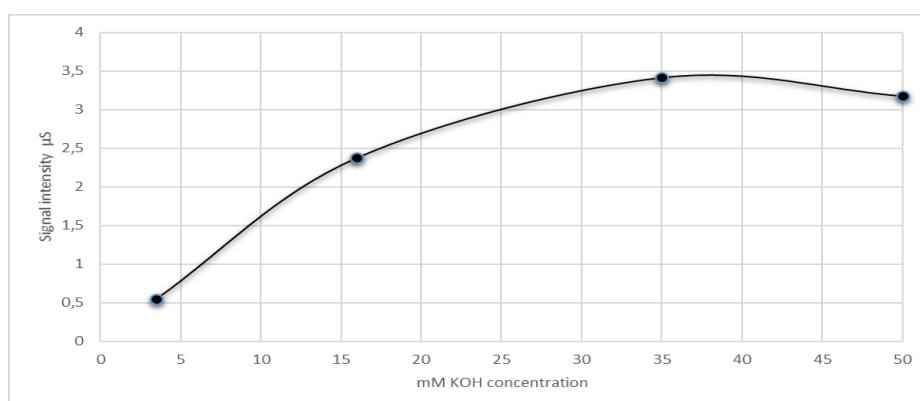


Figure 1. Signal evolution according to KOH mobile phase concentration

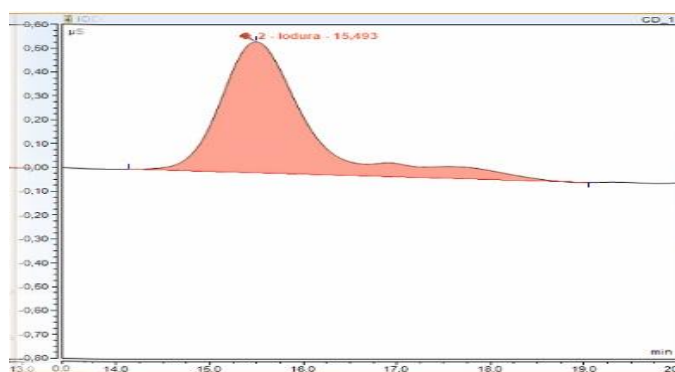


Figure 2. Chromatogram of iodide obtained at 3.5mM KOH eluent concentration

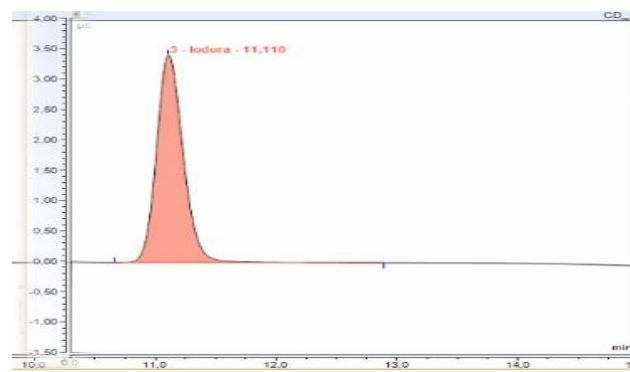


Figure 3. Chromatogram of iodide obtained at 35 mM KOH eluent concentration

3.2. The optimal flow rate of the mobile phase

Flow rate represents another important parameter to be tested whose value influences the amount of eluent in the column. As a result, the tests were performed at a different flow rate (0.6, 0.8, 1, and 1.5 mL/min) for optimizing the response and implicitly for obtaining a maximum signal. In this case, all tests were performed on a synthetic water sample containing 10 mg/L iodide to ensure a strong signal.

A flow rate of 0.6 mL/min has a 0.94 μS signal, the peak of the shape being highly distorted. As it could be noticed in Figure 4, the maximum signal response (3.825 μS) was recorded at a flow rate of 1.0 mL/min.

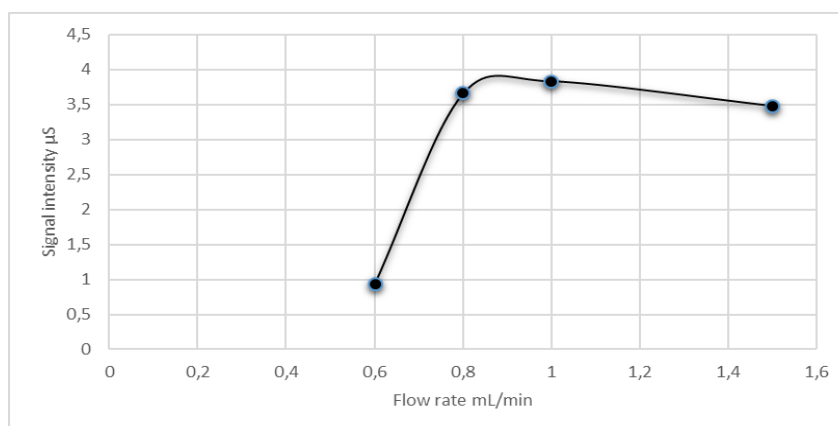


Figure 4. Signal evolution according to the mobile phase flow rate

3.3. Setting the optimum temperature

Another important parameter for the optimal setting of the ion chromatograph detector is the temperature set in the detector enclosure and column compartment. Since the conductivity depends on the temperature's value, the detector and column rooms are thermostated in to ensure measurements at a constant temperature. The experimental tests were performed at 25, 30, 35, and 40 $^{\circ}\text{C}$, respectively, by using a 10 mg/L iodide solution.

For a temperature set at 25 $^{\circ}\text{C}$ in the soft program of IC, no response from the detector was obtained corresponding to the iodide retention time chose for the separation column. Since no signal was recorded at this temperature, the parameter's value was increased up to 30 $^{\circ}\text{C}$, a signal of 2.73 μS being registered. The highest value of conductivity was obtained at 35 $^{\circ}\text{C}$, corresponding to a peak height of 3.48 μS (Figure 5).

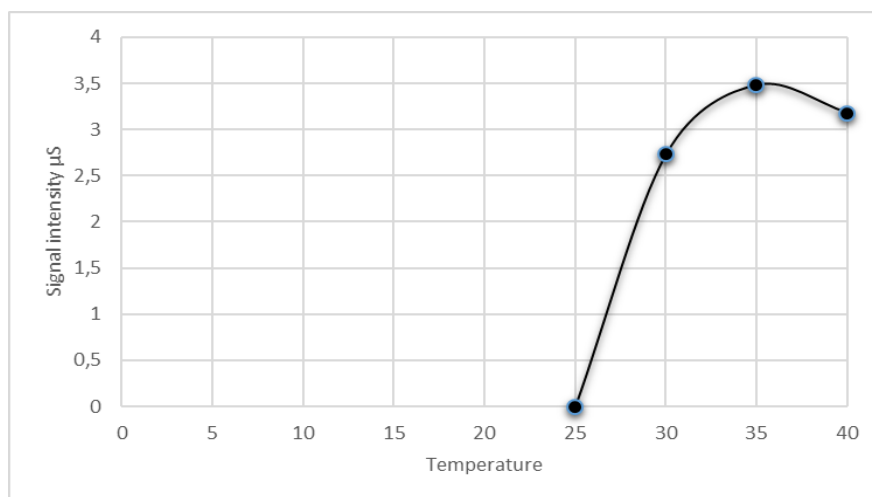


Figure 5. Signal evolution according to the temperature value

3.4. The optimum intensity of the suppressor current

Since the suppressor reduces the electrical conductivity of the eluent and implicitly the background, it is very important to set it to the optimal parameter. The electrolytic process takes place in the suppressor, and according to Faraday's electrolysis law, the current intensity is directly proportional to the mass deposited on the electrodes. The experimental tests have been performed at intensities of 50, 70, 87, and 100 mA, respectively.

At a 50 mA suppressor current, no signal of the analyte retention time was detected. As a result, the suppressor current was increased progressively, the highest signal (3.45 µS) being obtained at 87 mA. The evolution of the detector response according to the current intensity is shown in Figure 6.

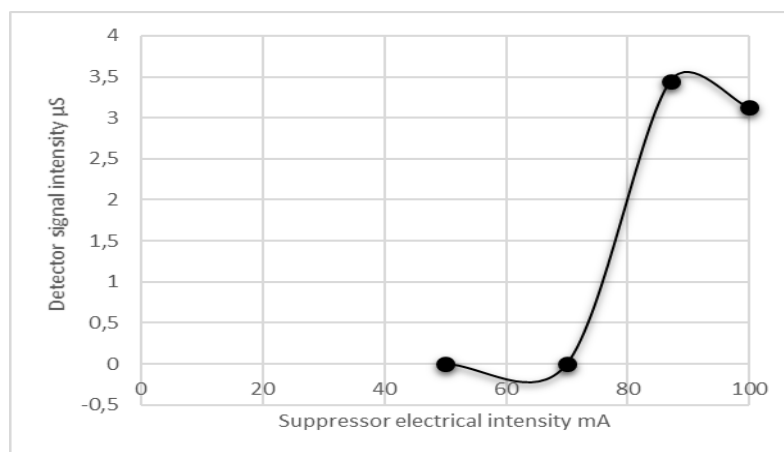


Figure 6. The response of the detector according to electrical intensity

The final settings performed after the optimization phase are presented in Table 2.

Table 2. Optimized parameters for iodide determination

Parameter	Eluent concentration	Flow rate of mobile phase	Temperature in detector chamber	Intensity of the suppressor current
Value	35 mM KOH	1 mL/min	35°C	87 mA

3.5. In-house validation experiments

In the first, the validation test followed the linearity property check, meaning the selection of the working field adequate to the iodine concentrations from underground water sources. The calibration curve involved iodine concentrations ranging between 2 and 10 mg/L (Figure 7). A homogeneity test of the dispersions for the lowest and highest iodine concentration from the selected working range (for 2 and 10 mg/L, respectively) was also performed.

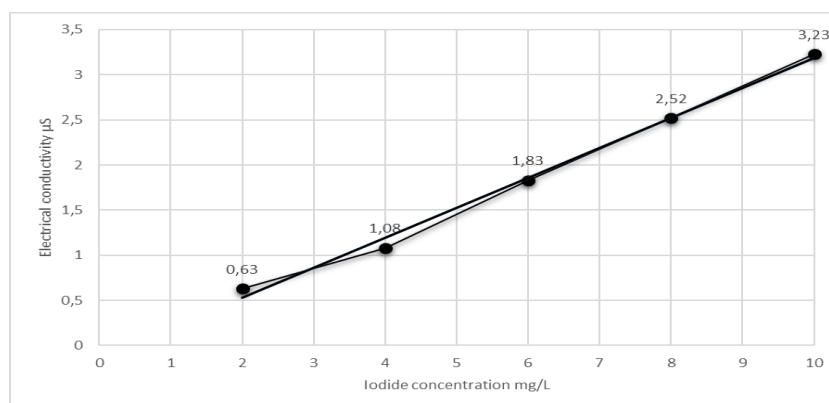


Figure 7. Calibration curve obtained for iodide using IC optimized method

The dispersions were tested using F (Fisher-Snedecor) test. The PG value was calculated and compared with the tabulated values of the distribution $F(f1, f2, 1-a)$, where $f1$ and $f2$ are the freedom degree and $1-a$ represents the confidence level. In this particular case, by analyzing 10 results, $f1$ and $f2$ were 9, and the confidence level was chosen to be 99%, F value being 5.35. If $PG < F$, the deviation between the dispersions is not significant, thus the calibration range is correctly chosen. If PG value is higher than F ($PG > F$), the dispersion test is significant and the range was incorrectly selected. The linearity results for the calibration curve and homogeneity of the dispersions are presented in Table 3 where (x_i) represents iodine concentration, (y_i) is the electrical conductivity, (a) is sensitivity, (b) represents the slope, (R) is the correlation coefficient, (S_y) , and (S_{x0}) means residual standard deviation and standard deviation, respectively, and (V_{x0}) is the variance coefficient of the method.

Table 3. Linearity results presented for the optimized method.

	x_i (mg/L)	2	4	6	8	10
Calibration Curve	y_i (µS)	0.63	1.08	1.83	2.52	3.23
Parameters		$y = -0.134 + 0.332x$				
		$a = -0.134$		$b = 0.332$		$R = 0.997$
		$S_y = 0.08$		$S_{x0} = 0.241$		$V_{x0} = 4.03\%$
<i>Test for the homogeneity of dispersions</i>						
	Y_{1i}	Y_{10i}				
	0.65	3.42				
	0.69	3.48				
	0.69	3.47		$(\text{Variance } y_1)^2 = 0.000284$ $(\text{Variance } y_{10})^2 = 0.000604$ $PG_{10/1} = 2.125$ $PG_{1/10} = 0.471$ $F(9,9, 99\%) = 5.35$ $PG < F(9, 9, 99\%)$ $2.125 < 5.35$		
	0.65	3.42				
	0.69	3.48				
	0.69	3.48				
	0.69	3.48				
	0.69	3.48				
	0.69	3.47				
	0.69	3.48				
	0.69	3.48				
	0.69	3.48				

Other performance parameters for the optimized method such as LOD, LOQ, precision, and recovery, could be found in Table 4. Obtained data emphasize that the proposed optimized method is appropriate for the determination of iodine in water sources, the accuracy value being 2.1% with a recovery of around 98%.

**Table 4.** In-house validation experiments.

<i>LOD, LOQ test</i>					
X_{measured} (mg/L)	0.672	0.688	0.686	0.670	0.649
	0.647	0.645	0.646	0.726	0.670
LOD (mg/L)	0.08		LOQ (mg/L)	0.26	
<i>Repeatability test</i>					
X_{measured} (mg/L)	6.14	6.13	6.07	6.03	6.01
	6.06	6.06	5.94	5.84	
$X_{\text{mean value}}$ (mg/L)	6.031		S (mg/L)	0.0936	
Repeatability (mg/L)	0.26		RSD_r %	1.55	
<i>Intermediate precision test</i>					
X_{measured} (mg/L)	6.14	6.13	6.07	6.03	6.01
	6.06	6.06	5.94	5.84	
	6.15	6.13	6.06	6.05	6.03
	6.06	6.07	5.92	5.85	
$X_{\text{mean value}}$ (mg/L)	6.033		S (mg/L)	0.126	
Intermediate precision (mg/L)	0.35		RSD_R %	2.09	
<i>Recovery test</i>					
Initial sample, $X_1=2$ mg/L	1.978	1.980	1.976	1.945	
	1.979	1.969	2.070	1.960	
Final sample, $X_2=4$ mg/L	3.955	3.950	3.967	3.970	
	3.917	3.891	3.960	3.920	
X_1 mean value (mg/L)	1.982	X_2 mean value (mg/L)	3.941	η(%)	97.96

3.6. The selectivity of the method, interference studies

The study of potential interferences is crucial in the validation process, as the presence of other elements in the water sources may influence the results of the analysis. Taking into account the separation column type, the abundance and frequency of the potential interactions, the following anions were studied: fluoride, chloride, sulfate, thiocyanate, thiosulfate, and carbonate.

-Fluoride, chloride, sulfate and thiocyanate influences on iodide determination

To investigate the influence of the mentioned above anions (excepting thiosulfate and carbonate), on iodide analysis, different concentrations of these anions were tested for the same concentration of iodide solution. The experimental data obtained from the performed tests are presented in Table 5.

Table 5. Recovery percentage for iodide in interference tests (I).

Fluoride concentration (mg/L)	Iodide concentration (mg/L)		Recovery yield (%)
	Added	Recovered	
0	6.009	5.91	98.4
3	6.009	6.02	100.2
10	6.009	6.23	103.7
15	6.009	6.22	103.5
Chloride concentration (mg/L)	Iodide concentration (mg/L)		Recovery yield (%)
	Added	Recovered	
10	5.91	5.95	100.7
40	5.91	5.76	97.5
80	5.91	5.57	94.2
Sulfate concentration (mg/L)	Iodide concentration (mg/L)		Recovery yield (%)
	Added	Recovered	
10	9.96	9.46	94.97
50	9.96	9.67	97.1
100	9.96	9.41	94.47
Thiocyanate concentration (mg/L)	Iodide concentration (mg/L)		Recovery yield (%)
	Added	Recovered	
10	10.07	9.12	90.06
25	10.07	9.12	90.06
50	10.07	9.43	93.64



These results indicate that fluoride concentration up to 15 mg/L, chloride values less than 80 mg/L, sulfate anions up to 100 mg/L, and thiocyanate values less than 50 mg/L does not influence the determination of iodide using ion chromatography technique. The highest recovery percentage was obtained in the case of fluoride, chloride, and sulfate anions addition (> 94 %).

- Thiosulfate and carbonate influence on iodide analysis

Unfortunately, the results indicated that the presence of thiosulfate and carbonate compounds in water samples has an important influence on iodide determination, as can be seen in Table 6.

Table 6. Recovery percentage for iodide in interference tests (II).

Thiosulfate concentration (mg/L)	Iodide concentration (mg/L)		Recovery yield (%)
	Added	Recovered	
10	9.88	9.36	94.74
25	9.88	8.27	83.7
50	9.88	81.27	822.6

Carbonate concentration (mg/L)	Iodide concentration (mg/L)		Recovery yield (%)
	Added	Recovered	
10	9.98	8.13	81.46
30	9.98	8.03	80.46
50	9.98	16	161.3

Thiocyanates concentration under 25 mg/L decrease the recovery rate of iodine, while a concentration of 50 mg/L conducted to aberrant results. The retention times for thiosulfate and iodide anions are very close, which can cause problems for ion separations at high concentration, the interference effect of thiosulfate being obvious.

In the case of carbonates, a concentration of up to 30 mg/L determined a low recovery yield of iodine (around 80%). Inadequate results of the recovery rate were also recorded for higher concentration value (50 mg/L). The conclusion emerging from these determinations indicates that carbonate has also a high influence in the analysis of iodide anion from water sources. As it was mentioned previously, the developed method was tested on a large number of samples of spring water, drinking water, underground, and surface water, Table 7 and 8 presenting the obtained results.

Table 7. Description of the collected water samples

Sample code	Description	Sample code	Description
GTW1	Geothermal water, Calimanesti, Spring no. 1	GW1	Groundwater, Rovinari, F2 point
GTW2	Geothermal water, Calimanesti, Spring no. 2	GW2	Groundwater, Rovinari, F3 point
GTW3	Geothermal water, Calimanesti, Spring no. 3	GW3	Groundwater, Rovinari, F4 point
MW1	Mineral water, Satu Mare	GW4	Groundwater, Rovinari, F11 point
SW1	Spring water, San Terra Crystal Spring	GW5	Groundwater, Deveselu
SW2	Spring water, San Terra Crystal Perle Spring	GW6	Groundwater, Chiajna, City Hall
SW3	Spring water, Miraqua, F5 source, Mostestea	GW7	Groundwater, Chiajna, School
SW4	Spring water, Calipso, F3 source, Fratesti	GW8	Groundwater, Chiajna, Stadium
SW5	Spring water, Calipso	GW9	Groundwater, district 2, Bucharest
SW6	Spring water, Cristal	GW10	Groundwater, Fountain North, Sfastofca, Tulcea
RW1	Raw water, Targu Carbunesti	GW11	Groundwater, F1, Costinesti
RW2	Raw water, Ticleni	GW12	Groundwater, F2, Costinesti
RW3	Raw water, Tezurenii	GW13	Groundwater, F3, Costinesti
RW4	Raw water, Floresteni, Tulcea	GW14	Groundwater, F4, Costinesti
RW5	Raw water, Pojogeni, Valea Rea	GW15	Groundwater, Dragiceni, Olt
RW6	Raw water, Scoarta Capacioasa, Tulcea	GW16	Groundwater, Celaru, Olt
RW7	Raw water, Scoarta Bobu, Tulcea	GW17	Groundwater, Ionesti, Valcea
RW8	Raw water, Ticleni	GW18	Groundwater, F1, Chemical Plant Raureni
RW9	Raw water, Babadag, Tulcea	GW19	Groundwater, F2, Chemical Plant Raureni
RW10	Raw water, Carcaleu, Tulcea	GW20	Groundwater, Well Pandeale, Dambovitia

**Table 8.** Iodide concentration in different types of water

Sample code	Iodide concentration (mg/L)	Sample code	Iodide concentration (mg/L)	Sample code	Iodide concentration (mg/L)
GTW1	0.38	GW5	0.48	GW19	<0.26
GTW2	3.86	GW6	<0.26	GW20	<0.26
GTW3	5.29	GW7	10.65	RW1	<0.26
MW1	0.78	GW8	0.87	RW2	<0.26
SW1	<0.26*	GW9	0.09	RW3	<0.26
SW2	<0.26	GW10	0.37	RW4	<0.26
SW3	1.25	GW11	<0.26	RW5	<0.26
SW4	0.76	GW12	<0.26	RW6	<0.26
SW5	<0.26	GW13	<0.26	RW7	<0.26
SW6	<0.26	GW14	<0.26	RW8	<0.26
GW1	0.32	GW15	<0.26	RW9	<0.26
GW2	<0.26	GW16	<0.26	RW10	<0.26
GW3	<0.26	GW17	<0.26		
GW4	<0.26	GW18	<0.26		

*LOQ of the optimized method.

4. Conclusions

An optimized ion-chromatography method for the determination of iodides from different types of water sources (surface water, groundwater, spring, and geothermal water) was developed and *in-house* validated. Several operational parameters such as eluent concentration (mobile phase, KOH), the flow rate of the mobile phase, the temperature in the detector chamber, and intensity of the suppressor current were optimized. The selectivity of the proposed method was tested, the influence of other anions (fluoride, chloride, sulfate, thiocyanate, thiosulfate, and carbonate) was also investigated. Meanwhile, fluoride, chloride, sulfate, and thiocyanate anions did not present interferences in iodide analysis, at the tested concentrations, unfortunately, it was shown that thiocyanates, as also carbonates lead to low recovery yields or even incorrect results.

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