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PROYECTO CICYT, HID 1999-0205

Salinización Asociada a la Precipitación y a las Aguas Subterráneas en distintas Áreas del Territorio Español Continental e Insular.

Ejecutor: IGME en coordinación con DIT/UPC

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Informe interno nº 1

Título:
"Errors involved in the analytical determination of the ratio Cl/Br"

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Resumen:

Para la ejecución del proyecto se ha adquirido y puesto a punto un sistema cromatográfico líquido aniónico de alta resolución (HPLC), para determinar con precisión el contenido en Br en agua y del Cl en aguas muy diluídas (agua de lluvia). Tanto el ión Cl como el Br se miden con un coeficiente de variación (CV) menor que 0,03 si hay más de 0,5 mg L^{-1} de Cl y más de 5 µg L^{-1} de Br. Para 1 µg L^{-1} de Br el CV es menor que 0,08. Así resulta que la relación Cl/Br se puede obtener con un CV normalmente de menos de 0,04, y de menos de 0,08 para agua con una relación muy alta.

Errors involved in the analytical determination of the ratio Cl/Br

1. General theory.

Let us consider the function y = f (x_i) in which the variable y depends on a set of independent variables x_i, all of them assumed normally distributed. Let $\bar{y}$ and $\bar{x}_i$ represent the mean value of the variables. Then:

$$\bar{y} = f(\bar{x}_i)$$

Be y = f (x_i) a given realization around the mean value. The difference to the mean can be approximated by a Taylor series, truncated at the first term:

$$\Delta y = y - \bar{y} \cong \sum f_i' \, \Delta x_i$$

In which

$$f_i' = \left(\frac{\partial f}{\partial x_i}\right)_{\bar{x}_i} \quad for\, x_i = \bar{x}_i , \quad and \quad \Delta x_i = x_i - \bar{x}_i$$

By squaring Δy

$$(\Delta y)^2 = \sum_i (f_i')^2 (\Delta x_i)^2 + \sum_{i \neq j} f_i' \, f_j' \, \Delta x_i \Delta x_j$$

The second term of the right-hand side contains covariance products that can be either positive, negative or zero.

If $\Delta x_i \,.\, \Delta x_j$ values are normally distributed, the second term of the right-hand side is zero. Then the standard deviation , σ, is:

$$\sigma_y^2 = \sum_i (f_i')^2 \sigma_{xi}^2$$

<u>Application to the Cl/Br ratio.</u>

For the R = rCl/rBr ratio, when the measured values of rCl and rBr are normally distributed for a given water sample:

$R = rCl/rBr = \alpha\, Cl/Br$

for Cl and Br in mg L^{-1} or µg L^{-1}; $\alpha = 80/35.5 = 2.253$.

Considering $\bar{R} = r\bar{C}l / r\bar{B}r = \alpha\, \bar{C}l / \bar{B}r$

$$\sigma_R^2 = \alpha^2 \left[\left(\frac{1}{\bar{B}r} \right)^2 \sigma_{Cl}^2 + \left(\frac{\bar{C}l}{\bar{B}r^2} \right)^2 \sigma_{Br}^2 \right] = \alpha^2 \left[\frac{\sigma_{Cl}^2}{Cl^2} + \frac{\sigma_{Br}^2}{Br^2} \right] = \bar{R}^2 \left[CV_{Cl}^2 + CV_{Br}^2 \right]$$

where CV = variation coefficient = standard deviation /mean. Thus

$$CV_R = \sqrt{CV_{Cl}^2 + CV_{Br}^2}$$

which is not affected by the factor α.

It results:

$$\sigma_R = \bar{R}\ .\ CV_R$$

Chloride and bromide analysis

For the chloride and bromide analyses in water samples, a high performance liquid (anionic) chromatographic system (HPLC) is used. The analytical column used is the IonPac AS9-HC in combination with the guard column AG9-HC. The eluent is Na_2CO_3 9 mM, at a flow rate of 1,25 mL. The detection system is supressed electrical conductivity. The injection loop capacity is typically 25-250 µL. For low concentrations of analytes, larger injection loops can be used to increase sensitivity, up to 2500 µL. Sample preparation for ion chromatographic analyses usually involves only a simple dilution and filtration of the sample. Due to large concentration differences between the major and minor components in a sample, they have to be analyzed in two different chromatographic runs using either different sensitivity settings on the detector or different dilutions of the sample. A complete chromatographic run lasts 17 minutes.

The detection limit is establised at 3S and the measurement limit at 10 S, being S the standard deviation of the calibration curve. For a lineal adjuntment expessed by Y = A + B X, in which

X is the peak area ($\mu S.cm^{-1}$. min) and Y the calculated concentration value of the reference sample, A the intercept and B the slope, it results:

Detection limit DL = A +35B
Quantification limit QL = A+105B

Chloride and bromide are isocratically separated and quantitated in the same water sample. Thus, if previous dilution is needed, handling errors does not affect the Cl/Br ratio. In no case there is interference between the Br peak and the nearby NO_3 peak. By measuring the electrical conductivity of the sample, the dilution to be carried out is calculated in order to obtain the right concentration for efficient measurement.

In the IGME the anion chromatograph is in operation since mid year 2000. Until march 2001 a small (0.25 mL) loop was used, which gives a reduced precision for Br in water samples optimized for Cl and SO_4 analysis. Afterward longer loops (0.5 to 2.5 mL) are in use to improve Br measurements.

There is not a complete series of tests to determine the analytical accuracy, but the laboratory of IGME has produced a set of calibration tests and repeated sample measurements from which the values of table 1 can be deduced (test data are not included).

Table 1.- Accuracy values for Cl, Br and SO_4 analyses. Actual values are equal or better than the figures indicated

	Cl mg/L	Br µg/L(3)	SO_4 mg/L
Detection limit	0.1 (1)	1 ; 2	0.02(2)
Quantification limit	0.3 (1)	3 ; 5	0.05(2)
Variation coefficient(4)	2%	2% ; 3%	0.5%

(1) Working in the range 0.1 to 5 mg/L; for the range 2.5 to 250 mg/L the values are 2 and 10
(2) Working in the range 0.2 to 10 mg/L; for the range 2.5 to 250 mg/L the values are 3 and 10
(3) First figure is for a long loop and the second for a short loop
(4) Estimation of the ratio of sample standard deviation to mean value. The variation coefficient deteriorates below the quantification limit.

The application to the R value (molar) gives table 2

Table 2. Orientative values of the variation coefficient for R (molar) and estimated value of its standard deviation, for sea water.

CV (Cl)	CV (Br)	CV (R)	R	σ	Comments (Cl in mgL; Br in μg/L)
0.02	0.02	0.028	563	15.8	Cl > 0.3; Br > 3
0.02	0.03	0.036	563	20.3	Cl > 0.3; Br > 5 (short loop)
0.1	0.1	0.41	563	79.6	Cl ~ 0.2; Br ~ 2 (4 for short loop)
0.2	0.2	0.28	563	158	Cl ~ 0.1; Br ~ 1 (2 for short loop)
0.5	0.5	0.71	563	400	Cl ~ 0.05; Br ~ 0.5 (1 for short loop)

This represents carefully prepared laboratory tests. Under service conditions actual results may be not so good due to deviating calibrating curves and unchecked small analytical circumstantes. More realistic values taking into account some sporadically repeated data are given on table 3:

Table 3.- Variation coefficients for Cl and Br

Cl (mg/L)	CV (Cl)	Br (μg/L)	CV (Br)
> 0.5	0.03	>2	0.05
> 0.5	0.03	>5	0.03
> 0.5	0.03	>1	0.08
~ 100	0.03	~ 100	0.03

This means that R can be determined with the following accuracy, for the usual range of values, as shown in table 4.

Table 4.- Practical values of the variation coefficient for R (molar) and estimated value of its standard deviation; long loop.

R	CV (R)	σ	Comments
563	0.06	34	Sea water value (close to)
300	0.04	12	Continental freshwater
1000	0.08	80	Polluted water
2200	0.04	88	Water with halite

Intercalibration results. The Laboratory Unit of the IGME periodically participate in intercalibration rounds with other laboratories by using certified samples. The results are in table 5. The results fron IGME differ 10% of certified values in mean and in the 64% of cases differ less than 3.6% for a level of Br between about 20 and 80 $\mu g\ L^{-1}$, which corresponds to weakly mineralized natural waters. This is in agreement with what has been deduced in the previous section.

Table 5.- Comparison among laboratories with certified samples from Aquacheck. Values of Br in $\mu g\ L^{-1}$.

N°	RV	ML	D	rd	LM	d	rd
1	42.60	42.73	+0.13	$+3.05.10^{-3}$	42.31	-0.29	$-6.81.10^{-3}$
2	72.30	71.03	-1.27	$-17.57.10^{-3}$	69.46	-2.84	$-39.28.10^{-3}$
3	39.30	38.22	-1.08	$-27.48.10^{-3}$	39.33	+0.03	$+0.76.10^{-3}$
4	21.80	23.88	+2.08	$+95.41.10^{-3}$	19.83	-1.97	$-90.37.10^{-3}$
5	41.50	42.93	+1.43	$+34.46.10^{-3}$	40.96	-0.54	$13.10.10^{-3}$
6	88.20	83.57	-4.93	$-55.71.10^{-3}$	87.49	-1.01	$-11.41.10^{-3}$
7	46.30	38.23	-8.07	$-174.30.10^{-3}$	46.96	+0.66	$+14.25.10^{-3}$
8	83.60	84.79	+1.19	$+14.23.10^{-3}$	86.50	+2.90	$+37.75.10^{-3}$
9	42.20	42.61	+0.41	$+9.72.10^{-3}$	42.55	+0.35	$+8.29.10^{-3}$
m				$-13.13.10^{-3}$			$-10.10.10^{-3}$
σ				$70.08.10^{-3}$			$35.88.10^{-3}$

RV = reference value
ML = mean of all laboratories
LM = laboratory mean (IGME)
D = difference (X-RV)
Rd = relative difference = d/RV
m = mean
σ = standard deviation
For ML rd = 1,3% ± 7,0%
For LM rd = 1,0% ± 3,6%