

Introduction

According to the Principle of Constant Proportions, the major components of seawater are not significantly influenced by biological processes, and changes in their concentrations, as a cause of chemical and geochemical processes, may occur on a long time scale. The composition in terms of minor constituents is also influenced by biological processes such as biodegradation, besides the change due to physical processes^{1,2}. Both classes of components can have their concentrations significantly changed in cases such of impact by coastal waters and by aquaculture practice due to biological contamination or water evaporation. In this work seawater samples have been analyzed by ion chromatography (IC) for ions F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻ and SO₄²⁻. A strategy was developed for the determination of ionic composition of seawater using the standard addition method, including test quality control. Measurement results are estimated by extrapolation of the internal calibration after performing standard additions with negligible uncertainty. Test quality control involves IC response linearity check, blank tests, duplicate measurements and the analysis of a synthetic sea water with known concentration.

Optimization of the measurement uncertainty by selecting standard addition range

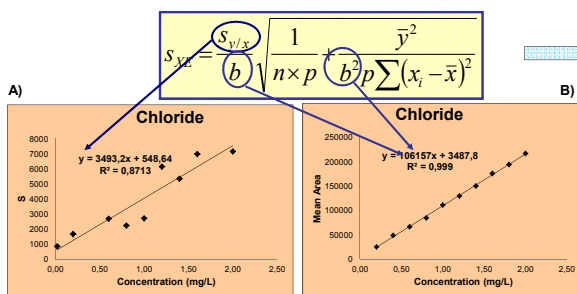


Figure 1: A) Standard deviation of the areas (for 6 replicate measurements per conc. level) vs. concentration of Cl⁻ in mg/L. B) Mean areas (for 6 replicate measurements per conc. level) concentration of Cl⁻ in mg/L.

$$F_{calc} \leq F_{tab} \Leftrightarrow \frac{s_2^2}{s_1^2} \leq F_{tab} \Leftrightarrow \frac{s_2}{s_1} \leq \sqrt{F_{tab}} \Leftrightarrow \frac{a+bx_2}{a+bx_1} \leq c \Leftrightarrow a+bx_2 \leq ac+cbx_1 \Leftrightarrow x_2 \leq \frac{ac-a+cbx_1}{b}$$

Condition to verify homogeneity of variances between the extreme points

x₁ - Conc. of diluted sample without standard addition;
x₂ - Conc. of diluted sample plus larger standard addition.

$$\frac{u_y}{y} = \sqrt{\left(\frac{u_{f_{dil}}}{f_{dil}}\right)^2 + \left(\frac{u_{f_{STD}}}{f_{STD}}\right)^2 + \left(\frac{s_{XE}}{x_E}\right)^2}$$

$$U_y = t \times u_y$$

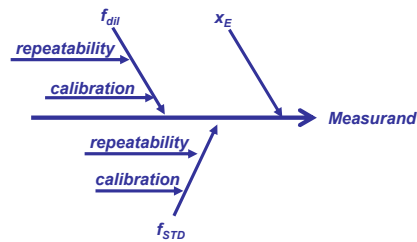


Figure 2: Cause-effect diagram for the determination of major and minor components in seawater.

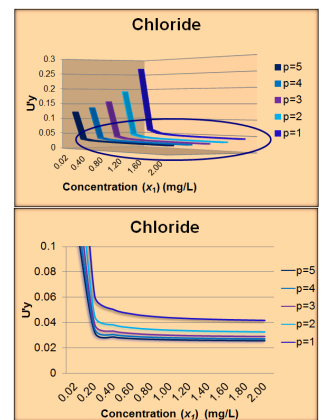


Figure 3: Relative expanded uncertainty (U_y) vs. concentration of Cl⁻ to evaluate the influence of the number of replicated injections of standard addition solutions (p).

From this study we obtained information to analyze samples:

- Number of replicated injections of solutions (p) needed to ensure a fit for intended use measurement uncertainty;
- Maximum concentration of analyte added (x₂-x₁) to the diluted sample (x₁), to obtain homogeneity of variances for the instrumental response;
- Sample dilution to concentration x₁, needed to ensure a fit for intended use measurement uncertainty.

Sample analysis & Quality control

Table 1: Relative standard uncertainty (u_i) of component i, and estimated measured quality value and expanded uncertainty for measurements of chloride for four seawaters (36A, 36D, 35A and 35D).

	36A	36D	35A	35D
u ^{f_{dil}}	0.011	0.011	0.011	0.011
u ^{f_{STD}}	0.007	0.007	0.007	0.007
s ^{s_{XE}}	0.043	0.080	0.042	0.043
u ^y (p=3)	0.045	0.081	0.049	0.050
C (mg/L)	15877	15673	15113	15906
U _y (k=2)	1407	2542	1486	1588

Quality Control

- Blank signal ≤ (3 × s_{y/x});
- Compatibility between the estimated and expected concentrations of all ions in artificial seawater

$$|x_{est} - x_{exp}| < 3 \times \sqrt{(u_{est})^2 + (u_{exp})^2}$$
- r (Pearson) ≥ 0.999;
- Absolute difference of x_E from duplicate and independent standard additions ≤ (2.8 × s_{XE})

Table 2: Expected and estimated concentrations for all ions in artificial seawater, recovery and compatibility test.

Ion	x _{exp} (mg/L)	x _{est} (mg/L)	R _{parameters}	x _{est} - x _{exp}	3 × √((u _{cest}) ² + (u _{cexp}) ²)
F ⁻	1.50	4.86	3.24	3.36	8.56
NO ₂ ⁻	10.00	19.90	1.99	9.90	16.04
Br ⁻	67.50	64.73	0.96	2.77	22.72
NO ₃ ⁻	207.00	191.25	0.92	15.75	51.77
SO ₄ ²⁻	501.13	485.59	0.97	15.54	93.22
Cl ⁻	19750.98	15932.68	0.81	3818.30	7668.53

Conclusions

- After selecting sample dilution that defines X₁, the maximum standard addition (X₂-X₁) is estimated, and, using model from Figure 3, U_y can be predicted;
- The developed QC strategy allows checking measurement performance including the estimated measurement uncertainty.

Bibliografia:

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- [2] N. Gros, M. F. Camões, R. B. Silva, Anal. Chim. Acta, 2010, 659, 85-92.