




Fluoride in beer by direct potentiometry and ion-specific electrode: Method assessment, validation, and application to commercial samples

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ABSTRACT

At present, beer is produced from the alcoholic fermentation of wort prepared with malt, barley or wheat and water, flavoured with hops. The main raw materials for producing beer are: water, barley, hops, yeasts. Unlike other alcoholic or distilled beverages, water is added during the preparation of the must. Consequently, in the mineral content of beer, the composition of the water is of great importance. Among the trace elements, fluoride, can be a common ion in water. This study describes and validates a potentiometric method, using an ion-selective electrode, to measure fluoride concentrations in the beer samples without preliminary treatments. The obtained detection limit (LOD) is 0.0006 mg L⁻¹ while quantification limit (LOQ) is 0.0017 mg L⁻¹. The standard addition method, used in this research, allows to obtain straight lines whose r² is higher 0.999. The sensitivity is very close to the theoretical one (59.16 mV at 25°C), in fact the electric potential varies by 55 ± 3 mV when the concentration differs by one order of magnitude. In an unusually low concentration interval 0.045 – 0.45 mg L⁻¹ acceptable precision and recoveries (<95 %) were obtained. The method was applied to 28 beer samples consumed in Sicilia (Italy) most of which were produced in other European countries having different alcoholic content. Fluoride concentration in the analysed samples was in the range 0.17–0.32 mg L⁻¹. The statistical treatment indicates a strong positive relationship between fluoride concentration and beer origin, indicating that this is closely related to the fluoride concentration. Conversely, alcohol content and beer type show a negative correlation with fluoride concentration. Considering all the analysed samples, the maximum value of the contribution to the diet corresponds to 3 %, obtained consuming 0.66 L of a lager beer produced in Italy.

1. Introduction

Historians say that beer was prepared from barley in Mesopotamia as early as 6000 B.C.E. Egyptian tomb paintings from 2400 B.C.E. show barley, or partially germinated barley, mixed with water and dried into cakes. The cakes were crushed and mixed with water, resulting in an extract that was fermented by microorganisms naturally present on the surfaces of the fermentation vessels (Young, n.d). Beer is the most widely consumed alcoholic beverage in local and international regions and is the third popular drink after water and tea (Eliaza et al., 2024). In 2021, per capita consumption in Europe was on average 67 L year⁻¹, the highest among all continents. Among the countries with the highest beer consumption, the Czech Republic is in pole position with 129 L year⁻¹, followed by Austria (101 L year⁻¹) and Poland (92 L year⁻¹). Germany is

only in fourth place with 89 L year⁻¹, while Italy, with its 35 L year⁻¹, is placed, together with France and Greece, in the last places of the ranking (Anonymous, 2023).

Currently, beer is obtained from the alcoholic fermentation of wort prepared with malt (often roasted or partially roasted), barley or wheat (or mixtures thereof) and water, flavoured with hops. The main raw materials for producing beer are: water, barley, hops, yeasts (*Saccharomyces carlsbergensi*, *Saccharomyces cerevisiae*). Unlike other alcoholic or distilled beverages, water is added during the preparation of the must. Consequently, in the composition of beer, especially for the flavour, the composition of the water is of great importance. In cheaper drinks, untreated tap water, probably, is used, while in other cases, water treated by ion exchange resins, through osmosis, etc. is used (Martín Delgado et al., 1992). The chemical composition of natural and drinking water,

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which includes various ions and trace elements, often gives rise to environmental and health concerns. Among the trace elements, fluoride, is a common ion in natural and drinking water. Fluoride is the thirteenth most abundant element in the world and constitutes from 0.06 % to 0.09 % of the earth's crust (Muthu Prabhu et al., 2023; V. Roshni, 2021). The most important sources of this anion in environmental and food matrices can be natural (volcanic emissions) or anthropogenic, using fluoride-based products (pesticides, chemical, etc.). As aerosols, fluoride can be transported over long distances by wind. Deposition can occur on soils or water surfaces (Paula Casagrande Marimon et al., 2007). In the soil fluoride exists mainly in the mineral form, in the atmosphere as hydrogen fluoride and in water, since it is soluble, occurs mainly in the form of fluoride ions, which is why it easily enters the food chain. In acid environments, such as those in the stomach, F⁻ can be converted to HF (Mendes et al., 2020). The HF can be easily absorbed, distributed and accumulated in the body (Mendes et al., 2020). Fluoride is of particular concern because it can have both therapeutic and adverse effects on human health, especially, in the case of children and infants (Kebede et al., 2016) due to the immaturity of the absorption and excretion systems. Fluoride is not considered an essential nutrient, it is generally accepted that in drinking water concentrations lower than 1 mg L⁻¹ are ideal to prevent tooth decay (Ayoob and Gupta, 2006). Excessive concentrations of fluoride in drinking water and beverages can lead to a number of adverse health effects, including dental and skeletal fluorosis, and can also cause neurological disorders in severe cases (Ling et al., 2022; Onipe et al., 2020). Fluoride food poisoning has been described in people consuming water and foods with high concentrations of this element. Cases of fluorosis have been reported in India following consumption of water and large quantities of tea, one of the main local beverages (Mahantesha et al., 2016), with high concentrations of fluoride. Some researchers (Veneri et al., 2023) argue that elevated fluoride intake has a negative effect on intelligence quotient levels in infants and young children. The World Health Organization (WHO) recommends a maximum fluoride concentration of 1.5 mg L⁻¹ in drinking water to avoid such health risks (WHO, 2022). However, in many parts of the world, natural and anthropogenic activities can result in elevated fluoride concentrations in groundwater sources, often exceeding recommended limits (WHO, 2022). In addition to drinking water, food and beverages are potential routes of F⁻ intake (Amorello et al., 2025; Karami et al., 2019). Other sources of exposure include dental care commercial products: toothpaste (1.0–1.5 g kg⁻¹), solutions and gels for topical treatment (0.25–24.0 g kg⁻¹) and fluoride tablets (0.25, 0.50 or 1.00 mg per tablet) (WHO, 2006). Scarce attention has been devoted to the determination of the fluoride in beers.

For the analysis of fluoride in water (NanoLab), the methods currently proposed by the IRSA-CNR (IRSA-CNR) (APAT, 2004; CNR, n. d.) and US Standard Methods (Water Research Institute - National Research Council) are UV-Vis spectrophotometry, ion chromatography and potentiometric (Ispra, 2021).

The determination of fluoride in beverages is a challenge for analytical chemistry (Amorello et al., 2025), given the complexity of the matrix and requires a technique with high accuracy, sensitivity and selectivity. Several methodologies have been developed so far for the analysis of fluoride in different matrices (Amorello et al., 2025; Cantoral et al., 2019; Jáudenes-Marrero et al., 2024; Karami et al., 2019) and, to our knowledge, there are few publications on the quantification, at trace levels, of fluoride in complex matrices such as beer (Jaudenes et al., 2018), considering that it contains hundreds of substances formed during production and in particular in fermentation processes. In this study we optimized and applied a simple and rapid method, based on potentiometry coupled with ion selective electrode, without mineralization process, in particular, the addition method used by us (even making a few additions) allows us to carried out directly on the sample by making the appropriate dilutions to quantify F⁻ in commercial beer samples.

Electrochemical techniques (voltammetry, potentiometry, etc.) are

the most frequently used in chemical analysis (Amorello et al., 2025; Amorello and Orecchio, 2021; Diana Amorello et al., 2023; Orecchio and Amorello, 2019). In potentiometry, the voltage difference between two electrodes is measured while the electric current between the electrodes is almost zero. The most widely used potentiometric methods, as in our case, use an ion-selective electrode (ISE) whose electric potential for a given ion in solution provides a highly specific analytical response. The versatility of the ion selective F⁻ electrode allows to use it over a wide concentration range, typically from 10⁻⁶ to 0.1 mol L⁻¹ (Otal et al., 2022), making it one of the most popular and convenient methods for fluoride ion determination (Konieczka et al., 2000). Fluoride ion-selective membrane electrodes are commercially readily available, inexpensive and easy to use, while other analytical techniques require expensive equipment and more technical assistance from highly trained and expensive personnel.

This study has been carried out considering the toxic effects in cases of chronic and high fluoride intake and the presence of this anion in beer. For this purpose, after optimizing the method, a direct analysis using an ion selective electrode is employed for the quantification of fluoride traces in 28 beer samples collected from the Italian market.

2. Experimental

2.1. Instrumentation

The measuring device involved a potentiometer (Crison, Modello GLP 22). The calomel electrode was used as reference, while, a membrane electrode called fluoride ion-selective electrode (Mettler-Toledo), was used as indicator electrode.

2.2. Chemicals

The standard NaF solution (90 mg L⁻¹) was ready by solubilizing 0.0498 g of the solid salt (previously desiccated in an electric oven at 105°C for 12 h and cooled and stored in a desiccator until ready to use) in 250 mL of deionized water. The obtained solution was stowed in a plastic bottle (APAT, 2004). The 5 M sodium hydroxide solution was obtained by solubilizing 50.0 g of NaOH in deionized water and making up to volume in a 250 mL flask. It's very important when a fluoride ion selective electrode is used, to control ionic strength and pH because this electrode measures the activity of the analyte rather than its concentration. TISAB (Total Ionic Strength Adjustment Buffer) solution, helps to maintain a constant ionic strength, preventing errors in the measurements. This solution, was prepared as described in a previous paper (Amorello et al., 2025) (114 mL of glacial acetic acid 96 % + 116.0 g of sodium chloride 99.5 % (Carlo Erba) + 4.0 g of trans-1,2- acid diaminocyclohexane-N,N,N,N-tetraacetic monohydrate 99 % to prepare 1 L of solution). The pH was adjusted to 5.0–5.5, adding sodium hydroxide solution 5 M. The diluted standard fluoride solution (9.0 mg L⁻¹) was prepared daily by diluting the concentrated fluoride standard solution with TISAB.

2.3. Quality assurance

The method has been validated, before applying to the beer samples, as already done in other cases (Amorello et al., 2022; Barreca et al., 2023; Di Gaudio et al., 2023) on the basis of linearity, precision, accuracy and LOD and LOQ.

The method was shown to be linear ($R^2 > 0.999$) in the range of 0.045–0.45 mg L⁻¹ of fluoride by making five/six additions of NaF standard (90 mg L⁻¹) to the TISAB solution (10 mL). The LOD and LOQ were estimated as three times and ten times signal/noise ratios, respectively. The precision was established by determining the intra and inter-day repeatability. To quantify the repeatability, analysis of fluoride solution, at known different concentrations, was completed three times on the same day. The inter-day repeatability was carried out

during 3 different days and each time with three replications. The recovery of fluoride was evaluated by spiking three beer samples (n° 2, 6, 22) with three concentration levels corresponding to 25 %, 50 % and 100 % of their initial concentration. The mean recovery values were obtained for the three independent replicates of the sample spiked. The recovery (%) was calculated by the formula:

$$\text{Recovery}(\%) = [(C_1 - C_2)/C_3] * 100$$

C_1 is the concentration determined in the fortified sample, C_2 the concentration determined in the unfortified sample and C_3 concentration relate to added standard.

The analyses of the real commercial samples, as in other cases (Amorello et al., 2025), were carried out after that the RT/F ratio, which appears in the electromotive force (e.m.f.) of Nernst Eq., was experimentally quantified, because the temperature at which the potentiometric determinations were carried out was almost constant but lower than 25°C, thus, it was incorrect to use the theoretical value of the RT/F ratio (59.16). For this intent, ten sequential adding (10 μL every time) of the standard fluoride solution (90 mg L^{-1}) were completed to 20.0 mL of a blank solution (TISAB solution), reading E and plotting it Vs $\log[F^-]$ after each addition (Fig. 1).

The high value of determination coefficient R^2 (0.9995) of the line obtained confirms the good linearity of the method. The slope of the straight line, in absolute value, represents the value of the RT/F ratio. Fig. 2 shows the Gran function correlated to the volume of fluoride standard solution added. The F^- concentrations in the commercial beer samples were calculated using the following equation:

$$[F^-] = \frac{C_0 V_0 + C_s V_s}{(V_0 + V_s)} \quad (1)$$

where C_0 represents the concentration of the beer sample; V_0 is the initial volume of sample beer; V_s and C_s correspond to the volume and the concentration of the standard fluoride solution used respectively.

$$G = (V_0 + V_s) \cdot 10^{\frac{E}{b}} = (C_0 V_0 + C_s V_s) \quad (2)$$

where E is the e.m.f. measured (mV) after each standard solution adding.

Using potentiometric measurements (titrations), Gran linearization, or Gran's plot, is an advantageous and creative method to quantify the unknown concentration of an analyte especially in the case of complex matrices as food and environmental. This method allows to acquire little data (before or after the end point) to localize it. Using the standard additions method, by extrapolating the straight line on the negative x-axis, ($G = 0$) it is possible to quantify the fluoride concentration in the potentiometric cell (C_0) using the Eq. (3):

$$C_0 = \frac{C_s V^*}{V_0} \quad (3)$$

V^* is the volume of standard fluoride solution required to have $G = 0$.

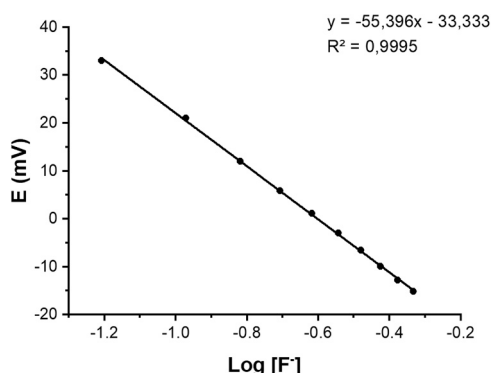


Fig. 1. Plot E (mV) Vs Log [F].

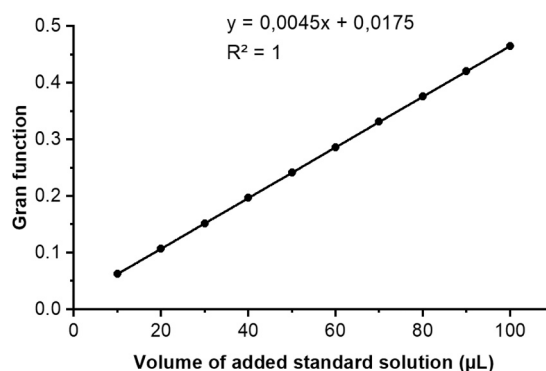


Fig. 2. Gran function Vs volume of fluoride solution added.

The analysis was repeated on seven blanks obtaining an average fluoride concentration of 0.015 mg L^{-1} .

2.4. Samples

A total of 28 very common and widely available national and international beer samples, among those most used by Italian consumers, were analysed. The beverages were purchased in different commercial supermarkets and markets on Sicily (Italy). The choice of beer types was made considering the most well-known and consumed ones. Their origin was taken into consideration, subsequently, for the data processing.

2.5. Analysis

The potentiometric quantifications were carried out on 10 mL of the sample stored in a plastic beaker to which 10 mL of TISAB solution was added. TISAB solution was added to eliminate possible interferences and adjust the ionic strength of the solution (Jáudenes-Marrero et al., 2024). Due to the complexity of the matrices, the standard addition method was used for all beer samples: six/seven additions (10 μL) of the standard fluoride solution (90 mg L^{-1}) were made to a known volume of sample, in particular, in the case of samples from preliminary tests assumed low fluoride concentrations, a 9.0 mg L^{-1} F^- solution was used. Waiting until the e.m.f. was constant before making a new addition. Plotting the Gran function against the volume of standard solution added, a straight line is obtained whose intercept on the negative volume axis corresponds to V_s . From this data, the fluoride concentration in the potentiometric cell can be calculated. As an example, Fig. 3 shows the Gran plot for a lager beer sample (n° 25), while Fig. 4 shows that of a red beer sample (n° 1) by the standard addition method.

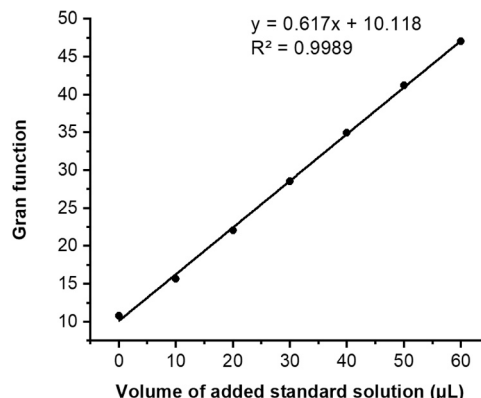


Fig. 3. Gran plot relative to a lager beer sample (n° 25).

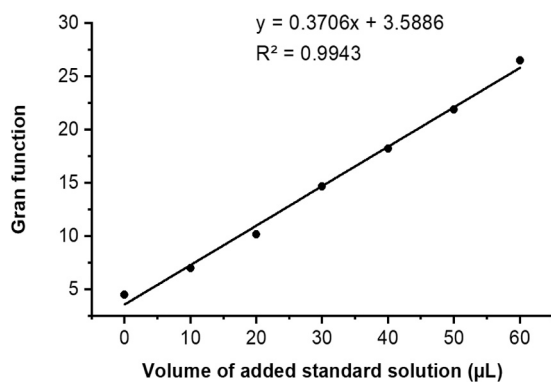


Fig. 4. Gran plot relative to a red beer sample ($n^{\circ}1$).

2.6. Statistical and chemometric

Statistical and chemometric approaches were used to gain a deeper insight into the contaminant profiles present in the analysed samples. PAST version 4.0 software, a free and widely used scientific data analysis tool, was used to process the data. For each sample, the alcoholic content, type and the origin indicated on the label were identified. At each type and beer origin, a value was assigned as shown in Table 1. Before carrying out the chemometric evaluations, the raw experimental data underwent a standardisation process. This involved adjusting each variable by subtracting its mean and dividing by the corresponding standard deviation. This processing ensures that all variables contribute equally to the analysis, regardless of their original scale.

3. Results

Considering that beer is a very complex matrices and contain high percentages of organic compounds, the use of standard addition method is very important. In this study, potentiometric method directly on beer sample was used. From the tests to evaluate the features of the analytical methods employed to quantify fluoride in beer samples, meanly, the recovery of enriched samples was about 95 %. The LOD value was 0.0006 mg L^{-1} and LOQ 0.0017 mg L^{-1} which are perfectly fine for the purpose of this research. All concentrations, relating to the 28 beer samples, quantified in this study are expressed in milligrams of fluoride per litre of beer (Table 2, Fig. 5). Also, Table 2 shows the mean fluoride concentrations (0.027 mg L^{-1}), the maximum (0.11 mg L^{-1}), the minimum (0.0055 mg L^{-1}) concentrations and the standard deviations (83 %). No maximum limit is set for fluoride in beers; however, taking into account the limit set at 1.5 mg L^{-1} for drinking water, none of the sample beers analysed exceed that limit.

In a previous study, Amorello et al. (2025) quantified fluoride in only

five different beer samples obtaining concentrations between 0.02 and 0.141 mg L^{-1} . The mean concentrations (0.081 mg L^{-1}) of fluoride reported in this work are compared to those found by several researchers (Fig. 6) (Jaudenes et al., 2018). As an example, Jaudenes et al. (2018) quantified the lower concentrations in beers from Belgium (0.06 mg L^{-1}), Germany (0.07 mg L^{-1}) and Spain (0.07 mg L^{-1}), while the same authors established that the highest concentrations corresponded to beers from the USA and Ireland, in which concentrations of 1.77 and 1.66 mg L^{-1} were quantified, respectively.

Researchers (Martín Delgado et al., 1992) tested 18 samples of beers consumed in the Autonomous Community of the Canary Islands, Spain, obtaining mean concentrations of 0.49 mg L^{-1} . Authors (Styburski et al., 2017) established that Polish beers were characterized by low mean F^- concentration (0.089 mg L^{-1}). The highest mean F^- concentrations were recorded in beers from Thailand (0.260 mg L^{-1}), Italy (0.238 mg L^{-1}), Mexico (0.210 mg L^{-1}), and China (0.203 mg L^{-1}).

3.1. Daily intake and health risks

The daily dietary exposure of a substance by a consumer depends on both the concentration of the substance in the food and the quantity consumed.

$$EDI(\text{mgday}^{-1}) = C \times V \quad (4)$$

where C and V, are the concentrations (mg L^{-1}) of fluoride in the beer and the quantity of it meanly consumed daily ($V_{\text{day}} \text{ L}^{-1}$) (0.66 L , a bottle) (Jaudenes et al., 2018), respectively.

The contribution (%) (Eq. 6) is calculated based on the EFSA reference value. The EFSA reference values used were adequate intake (AI) and upper-level intake (UL) (EFSA, 2024).

$$\text{Contribution}(\%) = 100 \times \frac{EDI}{\text{Reference value}} \quad (5)$$

The adequate intake is the amount of a mineral or nutrient that is assumed to be adequate for the needs of the population. The adequate intake amount for adult women is 2.9 mg/day and for adult men is 3.4 mg day^{-1} (EFSA). On the other hand, the upper-level intake for adults correspond to 7 mg day^{-1} and is the maximum chronic daily amount that can be ingested without risk to health. Considering all the analysed samples, the maximum value of the contribution corresponds to 3 %, obtained consuming 0.66 L of the sample $n^{\circ} 4$ a lager beer produced in Italy, which is negligible in relation to food safety regulations.

3.2. Statistical and chemometric considerations

The correlation matrix in Fig. 7 shows a strong positive relationship between fluoride concentration and beer origin, indicating that the

Table 1
Codes attributed for statistical treatment.

N°	Type	TYPE CODE	Origin	Origin CODE	N°	Type	TYPE CODE	Origin	Origin CODE
1	Red	10	IT	0	15	Blonde	2	PL	1
2	Blonde	2	PL	1	16	Blonde	2	DE	6
3	Blonde	2	FR	2	17	Blonde	2	DE	6
4	Blonde	2	IT	0	18	Blonde	2	IT	0
5	Blonde gluten free	5	IT	0	19	Blonde	2	IT	0
6	Red	10	NL	4	20	Blonde not filtered	1	IT	0
7	Blonde	2	NL	4	21	Blonde	2	IT	0
8	Blonde	2	SRB	5	22	Blonde	2	NL	4
9	Blonde	2	IT	0	23	Blonde	2	PL	1
10	Lime	15	PL	1	24	Blonde	2	IT	0
11	Blonde	2	DE	6	25	Blonde	2	NL	4
12	Dark	20	DE	6	26	Blonde	2	UK	7
13	Blonde gluten free	5	PL	1	27	Blonde	2	DE	6
14	Blonde	2	IT	0	28	Blonde	2	IT	0

Table 2
Samples description and fluoride concentrations.

N°	Alcohol %	Origin	Type	[F] mg L ⁻¹	N°	Alcohol %	Origin	Type	[F] mg L ⁻¹
1	5.4	IT	Red	0.070	15	4.5	PL	Lager	0.081
2	4.5	PL	Lager	0.063	16	4.7	DE	Lager	0.022
3	4.6	FR	Lager	0.16	17	0.5	DE	Lager	0.029
4	4.7	IT	Lager	0.32	18	5	IT	Lager	0.030
5	4.8	IT	Lager gluten free	0.058	19	4.7	IT	Lager	0.051
6	7.9	NL	Red	0.041	20	5	IT	Lager not filtered	0.058
7	10.5	NL	Lager	0.058	21	4.6	IT	Lager	0.044
8	0.5	SRB	Lager	0.13	22	5	ND	Lager	0.030
9	4.8	IT	Lager	0.083	23	9	PL	Lager	0.055
10	2	PL	Lemon	0.064	24	5	IT	Lager	0.11
11	4.9	DE	Lager	0.017	25	8.6	ND	Lager	0.13
12	4.9	DE	Dark	0.028	26	5.4	UK	Lager	0.021
13	4.2	PL	Lager gluten free	0.064	27	5	DE	Lager	0.22
14	4.6	IT	Lager	0.096	28	5	IT	Lager	0.13
Mean	0.027 mg L ⁻¹								
Min	0.0055 mg L ⁻¹								
Max	0.11 mg L ⁻¹								
SD	83 %								

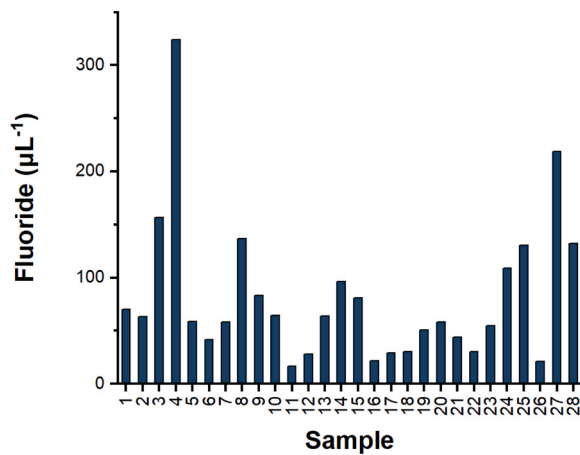


Fig. 5. – Fluoride concentration of beer samples.

origin of the samples is closely related to the fluoride concentration. Conversely, alcohol strength and beer type show a negative correlation with fluoride concentration. Overall, the data suggest that typological and geographical factors are key drivers in the variation of both fluoride concentration and alcohol percentage in the analysed samples. In this context, it can be assumed that the water quality, together with the relative types of water treatment systems, may influence the fluoride levels in the beer samples.

The biplot reported in Fig. 8 displays that the first two principal components, explains the majority of the variance in the dataset (Component 1 and Component 2 explain a cumulate variance of 68.2). While both alcohol content and beer type contribute significantly to the variance along component 1, both fluoride content and beer origin contribute significantly to the variance along component 2. Approximately 60 % of the samples are tightly clustered around the origin, indicating the similarity of the beer samples. The elliptical confidence region represents the typical sample distribution, with points outside the ellipse considered as outliers, which are likely to have different characteristics. In this context, the 96 % of the analysed samples can be clustered, taking into account a distribution of variables in the analysed samples, and only one sample is outside the elliptical.

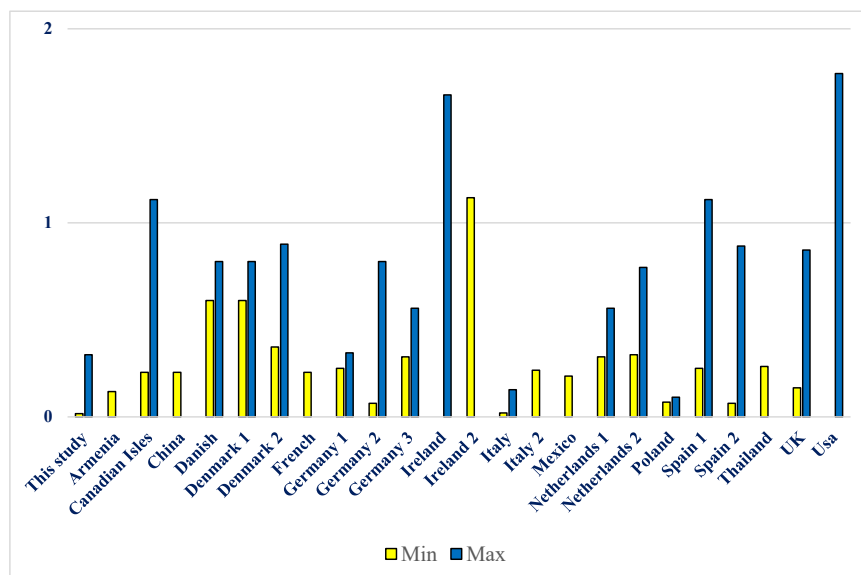


Fig. 6. Fluoride concentrations from different countries.

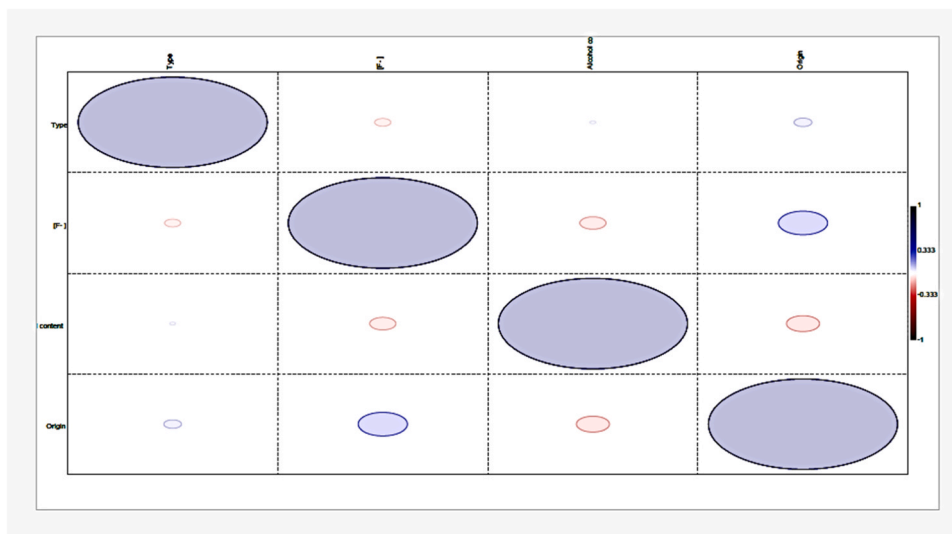


Fig. 7. Correlation matrix performed on type, Fluoride concentration, alcohol content and origin of analysed beer samples.

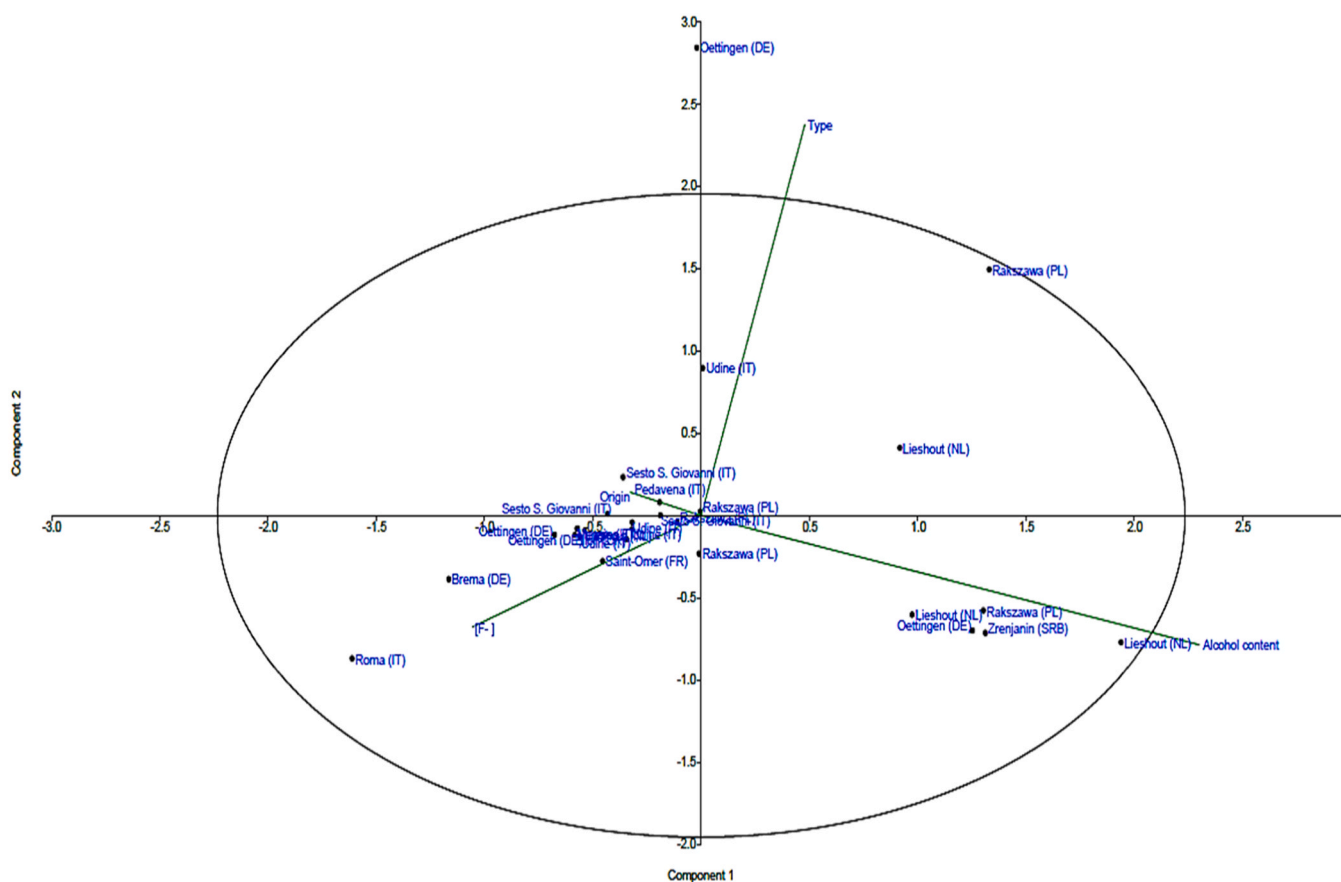


Fig. 8. Biplot performed on scaled data concerning type, Fluoride concentration, alcohol content and origin of analysed beer samples.

4. Conclusion

The main aim of this paper was to optimize a direct potentiometric method to quantify fluoride in a complex matrix as beer whose concentrations should be, theoretically, at ppb levels. Twenty-eight samples of different type (lager, red, dark gluten free, etc.) of national and international beers were investigated. Potentiometry is very advantageous to quantify trace components in these food matrices due to its high

sensitivity, accuracy, linearity, cost and speed. From the evaluation of the quality parameters, it is clear that the optimized methods used for beverage samples are quite satisfactory to assess any risks due to the consumption of the above beverage; however, it should be considered that, given the high sensitivity, it can be used for similar complex matrices of environmental interest, for the raw materials and for other foods. The potentiometric method for the quantification of fluorides, as in other scientific works (Rocha-Amador et al., 2023), can be used in the

evaluation of the quality of foods intended for children (Till et al., 2020), which are often prepared with waters whose fluoride content is higher than that permitted (Buzalaf et al., 2004). In all studied samples, fluoride concentrations were lower than those found in natural waters. The concentration of fluoride in ground water in the EU (EFSA) is usually low, but there are large regional differences due to different geological conditions. Surface water usually has a lower fluoride concentration than ground water, most often below 0.5 mg L^{-1} . The concentration of fluoride naturally occurring in drinking water in EU Member States ranges from 0.1 to ca. 6.0 mg L^{-1} , and shows large variation between and within countries (Ireland $< 0.01\text{--}5.8 \text{ mg L}^{-1}$, Finland $0.1\text{--}3.0 \text{ mg L}^{-1}$, and Germany $0.1\text{--}1.1 \text{ mg L}^{-1}$ (EFSA, n.d). European law on water for human consumption permits a maximum fluoride concentration of 1.5 mg L^{-1} . Considering the above, we can assume that fluoride in most beer samples depends on the agricultural products used but not on the water employed in the production process, since in the food industry, demineralized water is often used either by ion exchange resins or by reverse osmosis.

The high variability on the content of the element can be explained by the raw materials content and its origin, mainly because barley accumulate elements from the soil where the plants were growing while contamination during production processes is limited.

From the chemometric data it is evident that the fluoride concentration in the beer samples analyzed is strictly related to its origin, while the alcohol content is negatively correlated with the fluoride concentration. We can hypothesize that the water quality, together with the type of water treatment systems, can influence the fluoride levels in the beer samples. The high concentrations found by some authors in beers produced in the United States (mg L^{-1}) could be caused by the fact that fluoride is added to the drinking water of some states to prevent dental caries, while, probably, the situation is different in other geographical areas with endemic fluorosis, such as northern Mexico, South America and China.

Based on our data, the contribution of fluoride to the diet from beer intake with moderation does not pose health risks for adults, even if it is necessary to establish consumption recommendations in those areas where there are high concentrations of fluoride in the water supply or from other sources (toothpastes, mouthwashes, food supplements, etc.).

CRedit authorship contribution statement

Amorello Diana: Writing – original draft, Validation, Formal analysis, Conceptualization. **Silvia Orecchio:** Writing – original draft, Methodology, Formal analysis, Data curation. **Salvatore Barreca:** Writing – original draft, Validation, Software, Investigation, Data curation. **Giuseppe Arrabito:** Validation, Software. **Catanese Maria:** Investigation.

Declaration of Competing Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome. We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

We further confirm that any aspect of the work covered in this manuscript that has involved either experimental animals or human patients has been conducted with the ethical approval of all relevant

bodies and that such approvals are acknowledged within the manuscript.

We understand that the Corresponding Author is the sole contact for the Editorial process (including Editorial Manager and direct communications with the office). He is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs. We confirm that we have provided a current, correct email address which is accessible by the Corresponding Author.

Data availability

Data will be made available on request.

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