Alternative methods to quantify chloride ions as a variant to NC-ISO 2481

Métodos alternativos para cuantificar iones cloruros como alternativa a la NC-ISO 2481

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ABSTRACT

In this work, the volumetric, conductometric and potentiometric methods for the determination of Cl- ions in commercial NaCl samples were compared with the method established in NC-ISO 2481. $Hg(NO_3)_2$ was replaced by $AgNO_3$ as the titrant in the normalized method. The percentage of halogens expressed as Cl^-, NaCl, and I- were determined. The analysis performance parameters sensitivity, and repeatability were evaluated as precision and truthfulness criteria. One way Anova as carried out, where the Cochran C test was applied to verify the homogeneity of variance, with the p-Value = 0,82, which indicated the equality of the homogeneity of the same. The p-value show in ANOVA table is 0,99, and it was confirmed that there are no significant statistical differences between the means of the calculated percentage of NaCl.

Keywords: commercial NaCl, $AgNO_3$; determination of halides; alternative methods.

RESUMEN

En este trabajo se compararon los métodos volumétricos, conductimétricos y potenciométricos para la determinación de iones Cl- en muestras comerciales de NaCl con el método establecido en la NC-ISO 2481. Se reemplazó $Hg(NO_3)_2$ por $AgNO_3$

como valorante. Se determinó el porcentaje de halógenos expresados como Cl^-, I^- y NaCl. Los parámetros de rendimiento del análisis linealidad, sensibilidad y repetibilidad se evaluaron como criterios de precisión y veracidad. Se realizó un análisis de varianza de un factor, donde se aplicó la prueba C de Cochran para verificar la homogeneidad de la varianza, siendo el p-Value= 0.82, lo que indicó la igualdad de las varianzas. Con la Clasificación ANOVA Simple, el p-Valor=0,99 y se confirmó que no existen diferencias estadísticas significativas entre las medias del porcentaje calculado de NaCl.

Palabras clave: NaCl comercial, $AgNO_3$; determinación de haluros; métodos alternativos.

Recibido: 25/6/2023

Aprobado: 8/10/2023

Introduction

The production of salt in Cuba for human and industrial consumption avoids the country's annual imports of at least 60 million dollars. In addition to deliveries destined for families, NaCl is one of the main raw materials in the chemical industry. It is used in the national manufacture of a series of essential products, such as caustic soda or bleach, animal feed, dyeing of threads and fabrics, obtaining as benefiting the obtaining of dyes, reduction of chemical sequestrants due to its low levels of Ca^{2+} and Mg^{2+} (3 or 4 times lower than any other salt), etc. With the current manufacturing levels, the Geominero - Salinero Business Group (Geominsal) covers 99% of the internal demand and only 1% of the salt is bought abroad due to specific quality requirements.

The importance of Cl^- ion in a variety of chemical systems is indisputable. This makes it essential to develop analytical techniques that allow its quantification in a precise and exact way as well as reducing the cost of the analysis process as much as possible (1,2,3,4). The technique commonly used to quantify Cl^- ions is argentometry (5), however, other methods have been developed: turbidimetric (6), cyclic voltammetry (7), inductively coupled plasma-mass spectrometry (8), ESIs (9,10,11,12), technologies of microfabrication serigráfica (13), chromatography.(14,15,16)

There are several methods that allow the determination of Cl^- ions in different samples (17,18), for example, in the chemical industry, $Hg(NO_3)_2$ is used as a titrant for commercial NaCl samples, although other methods can also be used, of which it can cite: Mohr method, Volhard method, Fajans method, conductometric titration by precipitation, potentiometric titration by precipitation, coulometric titration by precipitation, among others.(19,20)

Arada and Yazdani-Pedram (10) reported a polymeric liquid membrane sensitive to Cl^- with a slope of -63,43±0,85 mV/dec, with a response interval of 10^{-6}-10^{-2} mol.dm^{-3} and a response time of 15 seconds. In addition, assemblies of analytical techniques have been carried out for the determination of Br^- and Cl^- in wastewater due to their toxicity.(19)

For the reasons explained above it is very important for the country to have recognized, fast, precise and exact methods with which quality control of commercial salt could be followed. Therefore, in this work the percentage of halogens expressed as Cl^- is determined by volumetric, conductimetric and potentiometric analysis methods with $AgNO_3$ as a titrant as an alternative to $Hg(NO_3)_2$, established as a titrant of NC-ISO 2481.(19)

Materials and methods

All the reagents described in this work were of pure quality for analysis (p.a). The materials and equipments used were certified and calibrated, suitable for use.

Preparation of commercial NaCl samples

To apply the volumetric, conductometric and potentiometric titrations, the commercial NaCl samples were subjected to a heat treatment in an oven at 105 °C for 2h to eliminate the solid's humidity. Then they were placed in a desiccator for 10 min.

0,015g of commercial NaCl was weighed and dissolved in a 1000ml volumetric flask and 50 ml of aliquot was taken for analysis.

In the case of the titrations, they were carried out with $AgNO_3$ whose additions were made with a micropipette.

Volumetric titration

The volumetric determination was carried out using the Mohr method.(21)

It is one of the best-known procedures for determining halides. In this method, a direct titration is carried out using an $AgNO_3$ solution as a titrant and a K_2CrO_4 solution as an indicator. The end point of the titration is detected by the appearance of the Ag_2CrO_4 precipitate (reddish in color) corresponding to the anion being titrated. It should be considered that if the pH is very basic, the AgOH will precipitate, which will later pass to the corresponding oxide, leading to an excessive consumption of Ag^+ ions in the titration according to the following reaction:

$$2Ag^+{}_{(aq)} + 2OH^-{}_{(aq)} \longleftrightarrow 2AgOH_{(s)} \longleftrightarrow Ag_2O_{(s)} + H_2O_{(l)} \quad (1)$$

On the contrary, an acid pH will cause a decrease in the sensitivity of the indicator and a certain delay in reaching the end, due to the decrease in the concentration of CrO_4^{2-} ions in the solution according to equilibrium:

$$2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \longleftrightarrow Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)} \quad (2)$$

The appropriate pH range for this method is between 7 and 10. Then, the analyte is quantified by mass measurement if its formula and that of the substance being weighed are known. The component to be determined precipitates from solution in the form of a sparingly soluble compound. Losses due to solubility will be negligible when the precipitate is separated by filtration and weighed after having been subjected to the necessary treatments. Bromide (Br^-), iodide (I^-) and cyanide (CN^-) ions cause a positive interference when valued as equivalent to Cl^-, S_2^-, SO_3^{2-} and $S_2O_8^{2-}$ ions, but can be removed by treatment of the sample with H_2O_2. PO_4^{3-} at concentrations higher than 25 mg/L precipitates in the form of Ag_3PO_4 and Fe above 10 mg/L masks the end point of the titration. Another drawback is the presence of color in the sample, which limits the application of the method to clear water with Cl^- concentrations greater than5 mg/L.(20)

The technique used was the following:

1. Pulverize the commercial NaCl sample.
2. Weigh 25g of the sample.
3. Dilute in volume of 250 ml.
4. Filter the solution and discard the residue.
5. Take 25 ml aliquot (triplicate).
6. Dilute in volume of 250 ml.

7. Add 1ml of K_2CrO_4 (5 %) and 90 ml of H_2O to a total of 100ml.
8. Take 10 ml of the solution.
9. Titrate with $AgNO_3$ (appearance of redbrick color precipitate).

Conductometric titration

Conductivity studies were carried out to evaluate the percentage of NaCl in commercial salt samples, for which a fixed concentration of 0,015 g (15mg/L) solutions of the commercial salt was used and $AgNO_3$ was used as a titrant whose additions were performed with a 150µL micropipette. It was observed that commercial NaCl solutions with a mass of 1g did not record conductivity measurements, due to the complexity of the matrix it is necessary to perform the analyzes with masses less than 1g. Using this instrumental method, a standard conductometric curve was obtained, with the aim of knowing the experimental conditions and thus determining the concentration of Cl^- ions by adding $AgNO_3$ as an alternative titrant, considering the conductivity of Cl^- with respect to the other ions involved. The experiments were carried out applying the volumetric and conductometric methods of analysis for a sample size (n=10) and in triplicate. The concentration of Cl^- ions was calculated using the following expressions, which were used in both methods:

$$C(Cl^-) = \frac{V(AgNO_3) \cdot C(AgNO_3)}{V(Cl^-)} \qquad (1)$$

$$\%(Cl^-) = \frac{m(Cl^-)}{m(sample)} \cdot 100 \qquad (2)$$

$$\%NaCl = \%Cl^- \cdot Fg\left(\frac{Cl^-}{NaCl}\right) \qquad (3)$$

Potentiometric titration

Through potentiometric titrations, the Cl^- and I^- ions and the percentage of NaCl in samples of commercial salt were determined simultaneously. For this, a fixed concentration of the solutions of the commercial salt of 0,015 g (15mg/L) and $AgNO_3$ was used as a titrant agent whose additions were 90 µL using a 100µL micropipette.

The concentration of Cl- ions could be determined by adding $AgNO_3$ as an alternative titrant, and Cl^- and I^- were determined simultaneously considering the values of the constants of the solubility product:

Kps (AgI) = $4{,}5 \cdot 10^{-16}$ Kps (AgBr) = $6 \cdot 10^{-13}$ Kps (AgCl) = $1{,}8 \cdot 10^{-10}$

The experiment for a sample size took effect (n= 10) and in triplicate. The concentration of ions Cl calculated intervening following expressions himself:

$$E = E^{o} \pm \frac{0{,}059}{n} \log \frac{[Ox]}{[Red]} \qquad (4)$$

$Ag^{+}_{(aq)} + e^{-} = Ag_{(s)}$ $E^{o} = 0{,}558$ V (indicator reaction) (4)

$E_{ind} = E^{o}_{AgI/I} + 0{,}059 \log [I^{-}]$ $E^{o} = -0{,}15$ V (5)

$E_{ind} = E^{o}_{AgCl/Ag} + 0{,}059 \log [Cl^{-}]$ $E^{o} = 0{,}22$ V (6)

$E_{ind} = E^{o}_{Ag+/Ag} + 0{,}059 \log [Ag^{+}]$ (7)

Evaluation of ions mixtures

When a mixture of several ions capable of precipitating with the same reagent is titrated, if the solubilities are sufficiently different, they can be titrated successively. If the titration of a mixture of Cl^{-}, Br^{-} and I^{-} 0.1 M with Ag^{+} (0.1 M) is considered, a case is considered of interest because the Ag^{+} ion is a poorly selective precipitating agent, and sometimes-simultaneous precipitation occurs. Figure 1 shows the titration curves obtained from the logarithmic diagram, which served as a tool to explain the results obtained later. The diagram has been constructed considering the following values for the solubility products: AgCl=10^{-10}; AgBr=10^{-13}; AgI=10^{-16}. It is observed in Figure 1 that from pAg^{+} =11 the simultaneous precipitation of AgI and AgBr takes place and from pAg^{+}=9 the three halides of Ag precipitate simultaneously. Likewise, in the titration curves for I^{-} and for Br^{-} the equivalence point is not reached.

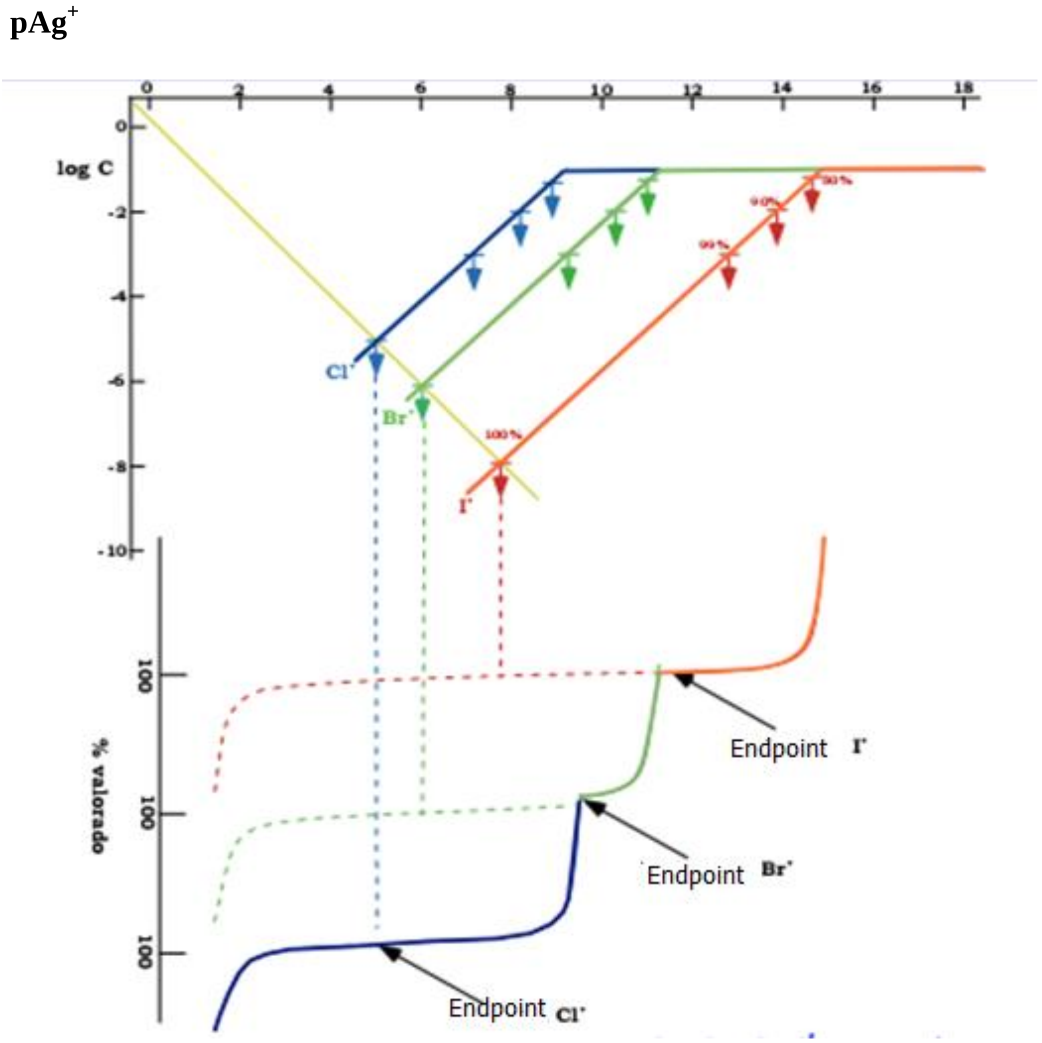


Fig. 1-Theoretical titration curves for Cl^-, Br^- and I^- (10^{-1} M) with Ag^+

The errors that are obtained due to this are the following:

Iodide titration:

$$E_r = \frac{[Ag^+]_f - [I^-]_f}{C_i} \cdot 100 = \frac{10^{-11} - 10^{-5}}{10^{-1}} \cdot 100 = -0{,}01\% \quad (8)$$

But, $[Ag^+]_{total} = [Ag^+] + AgI_{(s)}$+ complexes ≈ $[Ag^+]_{end}$ (en dissolution).

$[I^-]_{total} = [I^-] + AgI_{(s)}$ + complexes ≈ $[I^-]_{end}$ (in solution).

Bromide titration:

$$E_r = \frac{[Ag^+]_f - [I^-]_f}{C_i} \cdot 100 = \frac{10^{-9} - 10^{-8}}{10^{-1}} \cdot 100 = -1\% \qquad (9)$$

Chloride titration: Cl^- is perfectly titrated with its equivalence point. In any case, in precipitation reactions, happens in practice may be different due to a multitude of physical phenomena theoretically expected. For example, at the first equivalence point there is AgI (s) + Br^-, but the AgI precipitate can adsorb other species present in solution. On the other hand, the colloidal aspect of the precipitates must be considered. Thus, I^-, because of its very small solubility product, rarely titrates with Ag^+, facilitating colloid formation. The experimental facts exposed before are corroborated in Figure 2 and the equivalence point is verified.

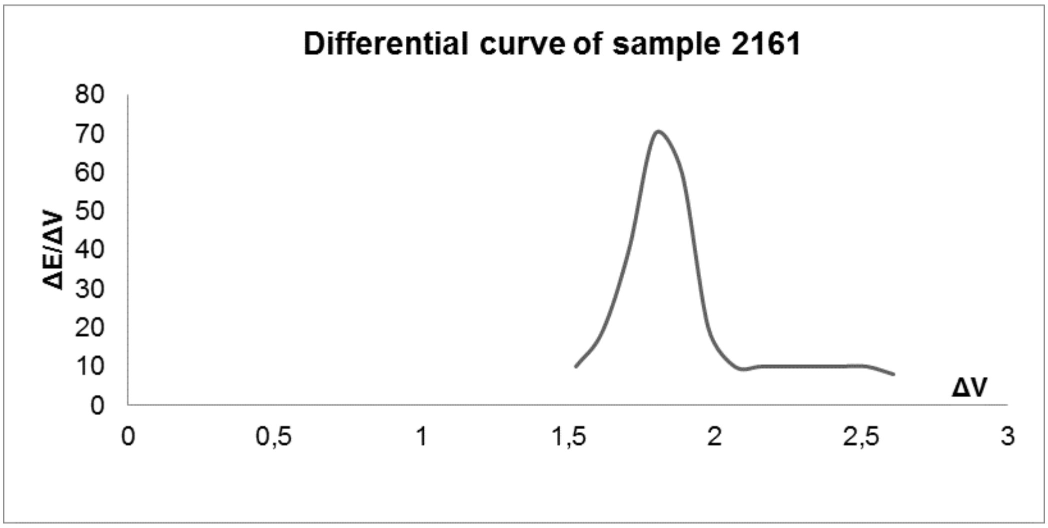


Fig. 2- Differential curve of chloride

The differential curve takes its maximum at coordinates (1.84; 70), this is the total equivalence volume due to the fact that in the sigmoid curves in the potentiometric titration of commercial NaCl samples two jumps are evidenced, that is, two points of equivalence (see Figure 3), at the equivalence point for I^- simultaneously leaves Br^- and the second for Cl^-. Through the differential curve, it was verified that the first moment is not defined because I^- and Br^- do not reach their equivalence volume, but the equivalence volumes of I^- and Cl^- obtained experimentally were used to know the concentrations of these species.

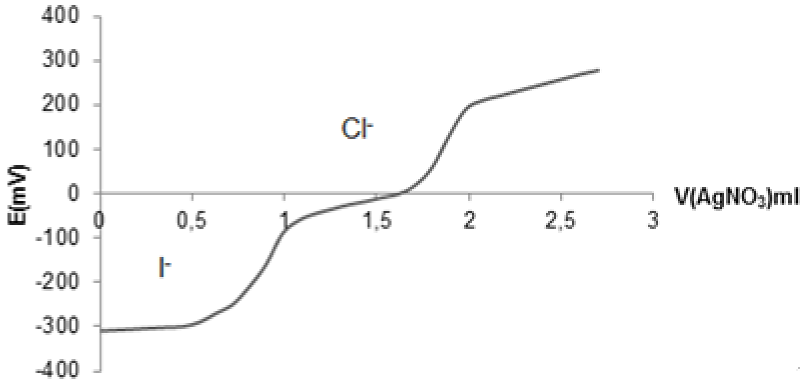


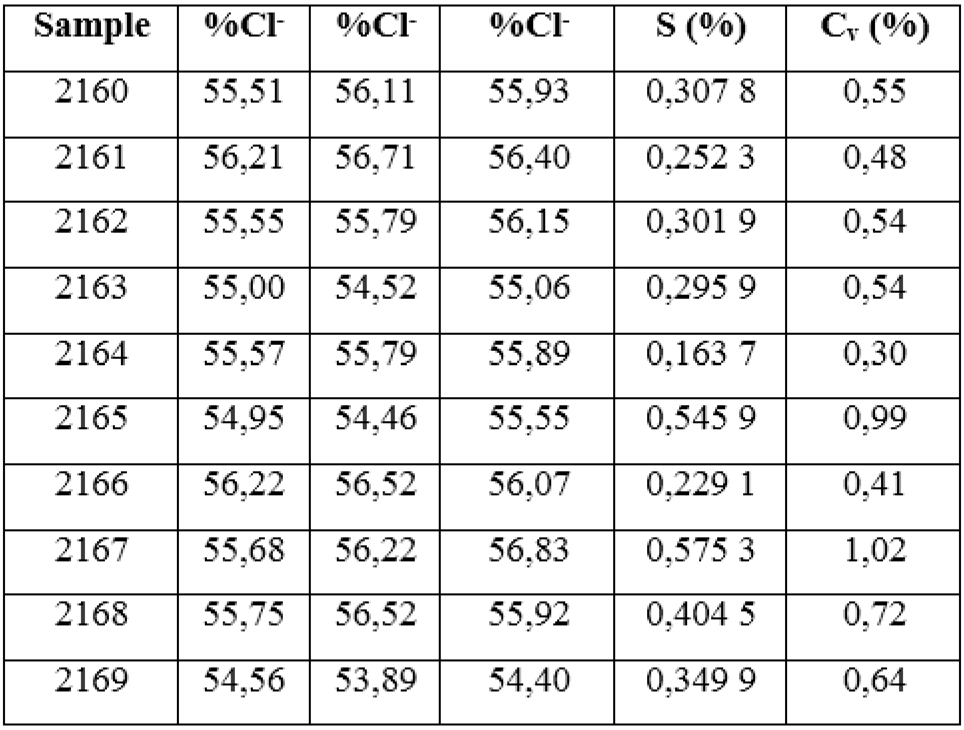
Fig. 3- Potentiometric titration of a mixture of I^- and Cl^- with $AgNO_3$ 0,099 mol/L

All the processing of results and the statistical tests were carried out using the Statgraphics Centurion XV software, Microsoft Office Excel 2016.(21, 22)

Results and discussion

The standardized method was taken as a reference to establish comparisons with the proposed alternative methods. Tables 1 and 2 show the results of the percentage of halogens expressed as Cl^- and the percentage of NaCl of the samples obtained by the volumetric method using $Hg(NO_3)_2$ as titrant, processed in triplicate.

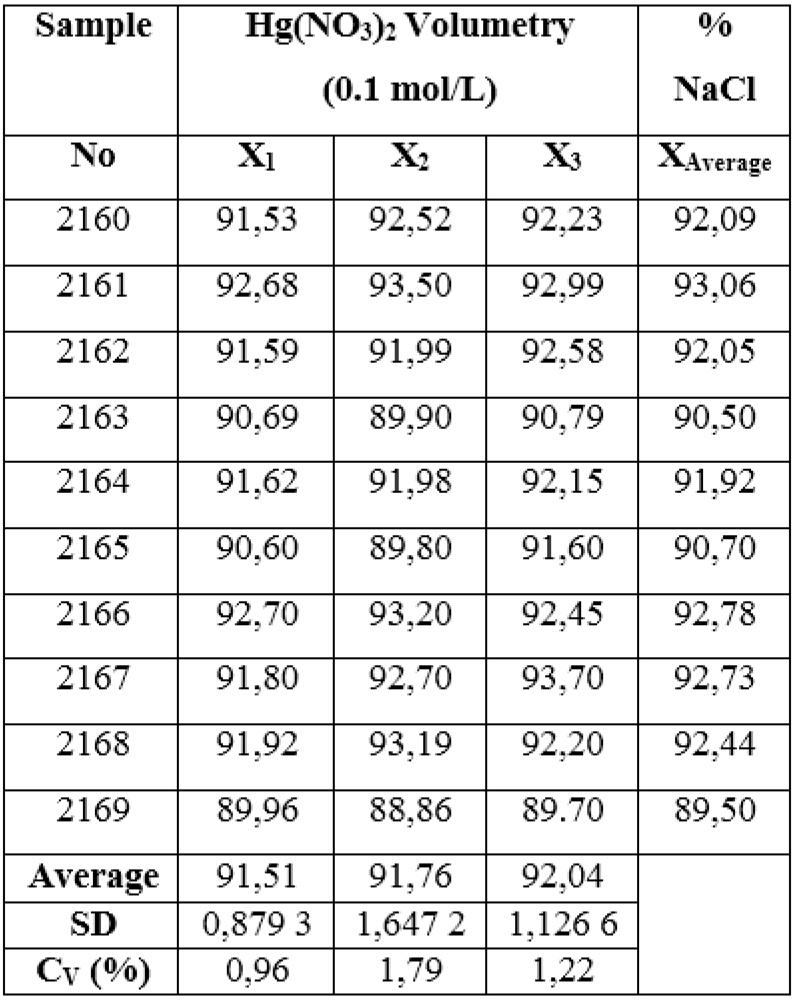
Table 1. Percent of halogens expressed as Cl^- with $Hg(NO_3)_2$ volumetry.



Sample	%Cl^-	%Cl^-	%Cl^-	S (%)	C_v (%)
2160	55,51	56,11	55,93	0,307 8	0,55
2161	56,21	56,71	56,40	0,252 3	0,48
2162	55,55	55,79	56,15	0,301 9	0,54
2163	55,00	54,52	55,06	0,295 9	0,54
2164	55,57	55,79	55,89	0,163 7	0,30
2165	54,95	54,46	55,55	0,545 9	0,99
2166	56,22	56,52	56,07	0,229 1	0,41
2167	55,68	56,22	56,83	0,575 3	1,02
2168	55,75	56,52	55,92	0,404 5	0,72
2169	54,56	53,89	54,40	0,349 9	0,64

When analyzing repeatability as a precision criterion, it is observed that the coefficients of variation (CV) obtained are very low and there is little dispersion in the analyzes. (Table 2).

Table 2. NaCl percentage results from commercial NaCl samples.



Sample	$Hg(NO_3)_2$ Volumetry (0.1 mol/L)			% NaCl
No	X_1	X_2	X_3	$X_{Average}$
2160	91,53	92,52	92,23	92,09
2161	92,68	93,50	92,99	93,06
2162	91,59	91,99	92,58	92,05
2163	90,69	89,90	90,79	90,50
2164	91,62	91,98	92,15	91,92
2165	90,60	89,80	91,60	90,70
2166	92,70	93,20	92,45	92,78
2167	91,80	92,70	93,70	92,73
2168	91,92	93,19	92,20	92,44
2169	89,96	88,86	89.70	89,50
Average	91,51	91,76	92,04	
SD	0,879 3	1,647 2	1,126 6	
C_V (%)	0,96	1,79	1,22	

Determination of the percentage of commercial NaCl, comparison of the methods

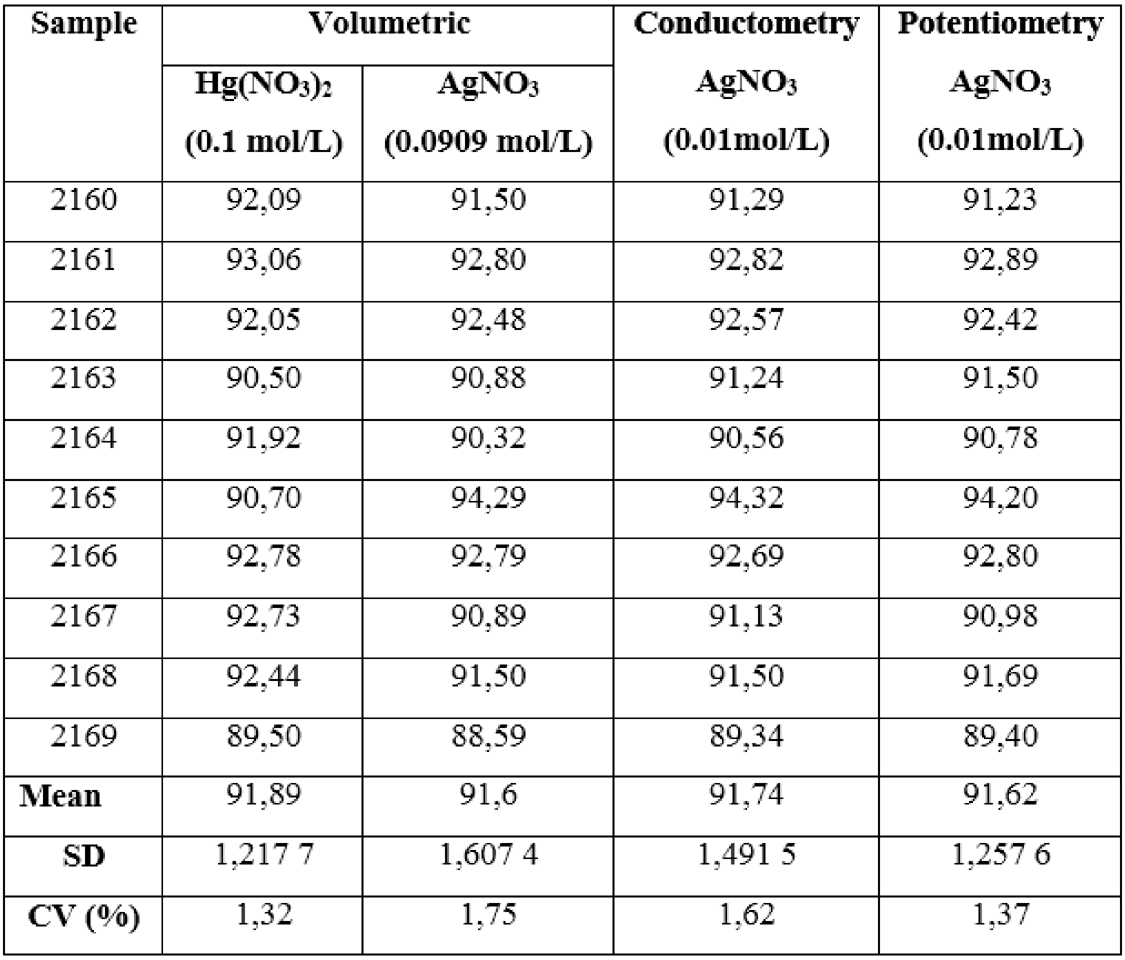
Table 3 shows the means of the percentages of NaCl obtained in the analyses, carried out in triplicate for the standard method and those proposed as an alternative method.

As it could be observed in the analyses, the potentiometric and conductometric titrations show very good precision, as well as the volumetric titration with $AgNO_3$, which shows that the alternative methods with $AgNO_3$ have good correspondence to the results obtained with the standardized method with $Hg(NO_3)_2$ (13) , which show good precision and little dispersion in the analyses.

The instrumental methods applied to monitor the quality control of commercial salt showed good performance in the analysis, which is demonstrated in the results obtained.

With the potentiometric method applied, the potentiometric curves were obtained and in this way the volume of equivalence of I^- and Cl^- were determined simultaneously in the samples. A representative curve of the obtained results is shown (Figure 3).

Table 3. Results of the NaCl percentage of commercial NaCl samples.



Sample	**Volumetric**		**Conductometry**	**Potentiometry**
	$Hg(NO_3)_2$ (0.1 mol/L)	**$AgNO_3$ (0.0909 mol/L)**	**$AgNO_3$ (0.01mol/L)**	**$AgNO_3$ (0.01mol/L)**
2160	92,09	91,50	91,29	91,23
2161	93,06	92,80	92,82	92,89
2162	92,05	92,48	92,57	92,42
2163	90,50	90,88	91,24	91,50
2164	91,92	90,32	90,56	90,78
2165	90,70	94,29	94,32	94,20
2166	92,78	92,79	92,69	92,80
2167	92,73	90,89	91,13	90,98
2168	92,44	91,50	91,50	91,69
2169	89,50	88,59	89,34	89,40
Mean	91,89	91,6	91,74	91,62
SD	1,217 7	1,607 4	1,491 5	1,257 6
CV (%)	1,32	1,75	1,62	1,37

With the conductometric method, a standard curve was obtained to know the experimental conditions and to obtain the equivalence volume, as is shown (Figure 4).

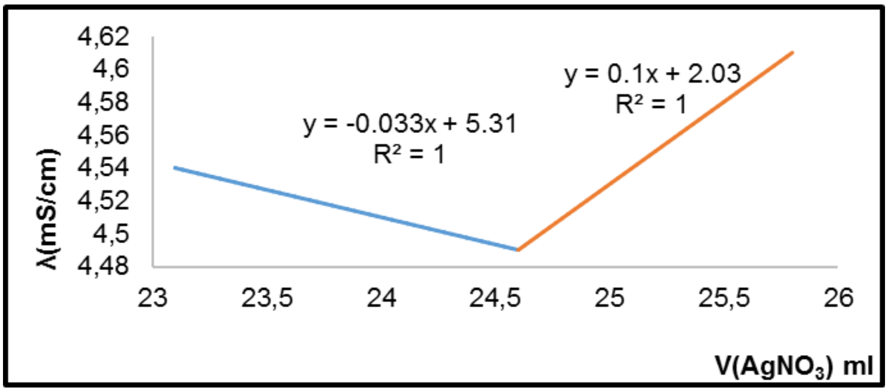


Fig. 4- Standard conductometric curve of the NaCl samples

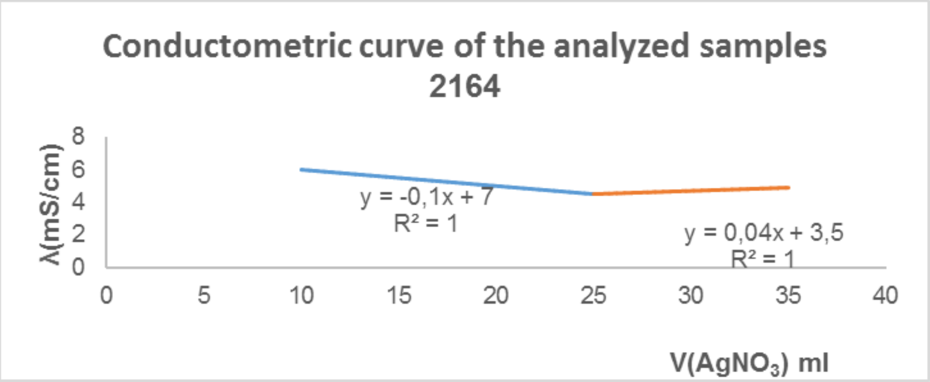


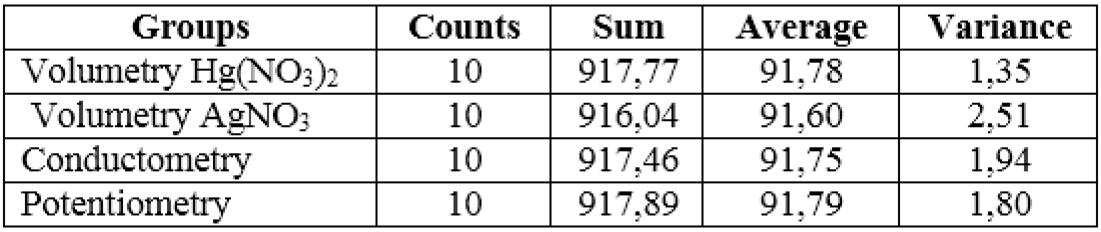
Fig. 5- Representative conductometric curve of the analyzed samples

As can be seen from Figure 5 the equivalence volume obtained in the samples analyzed was 25 ml.

The instrumental methods applied (10) to monitor the quality control of commercial salt showed good performance in the analysis, which is demonstrated in the results obtained.

With these results, the comparison of the methods was made. A one-factor analysis of variance was performed, and the results appear in Table 4. The variance contrast performed by the Cochran's test was 0,33 for a P-value of 0,82, higher than the significance level (α =0, 05) which indicates the equality of variances of the four contrasted methods for 95 % confidence.

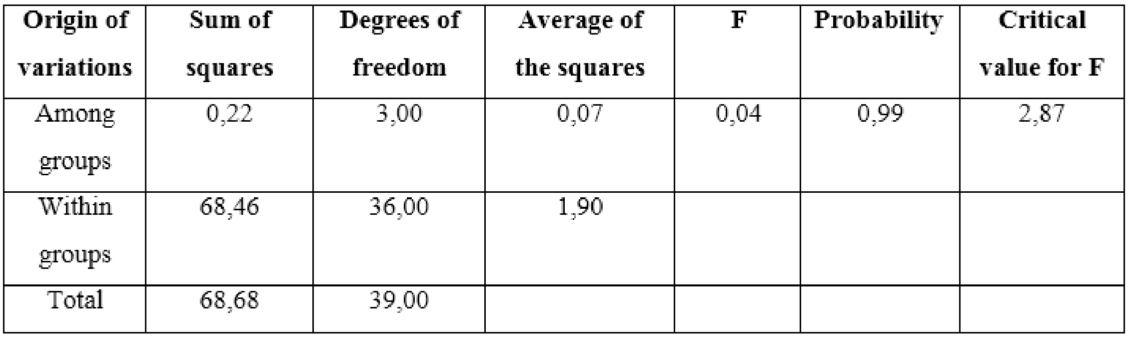
Table 4. One factor variance analysis.



Groups	Counts	Sum	Average	Variance
Volumetry $Hg(NO_3)_2$	10	917,77	91,78	1,35
Volumetry $AgNO_3$	10	916,04	91,60	2,51
Conductometry	10	917,46	91,75	1,94
Potentiometry	10	917,89	91,79	1,80

Once the homogeneity of the variances was verified, a Simple Classification Analysis of Variance was performed; the results are shown in Table 5.

Table 5. Analysis of Variance of Simple Classification.



Origin of variations	Sum of squares	Degrees of freedom	Average of the squares	F	Probability	Critical value for F
Among groups	0,22	3,00	0,07	0,04	0,99	2,87
Within groups	68,46	36,00	1,90			
Total	68,68	39,00				

As observed in the simple classification ANOVA table, the calculated F(Fisher) value is lower than the experimental F value, so the null hypothesis that there are no statistically significant differences between the means of the determinations of the four methods can be accepted. Contrasted methods using $AgNO_3$ or $Hg(NO_3)_2$ as titrants for 95% confidence, with the p-Value equal to 0,99, which is higher than the significance level (α =0,05).

Conclusions

The percent of halogens expressed as Cl^- and the percentage of NaCl obtained in the alternative methods with $AgNO_3$ turned out to be very similar to the results obtained with $Hg(NO_3)_2$ as established titrating agent. The performance parameters analyzed showed good performance, especially the instrumental methods followed by the volumetric one with the alternative titrant, which is corroborated by the obtained results. It was found that there are no statistically significant differences between the means of the determinations of the percentage of NaCl calculated using $Hg(NO_3)_2$ and $AgNO_3$ as titrant, respectively when comparing the four methods for 95% confidence.

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Conflicts of interest

The authors declare no conflicts of interest regarding the publication of this paper.

Authors contribution

María of Ángeles Arada Pérez: Conception and design metodológico of investigation. Realization of active participation in the discussion of the results to be. Revision and approval of the final version of work.

Leandro León Duharte: Conception and design metodológico of investigation. Revision and approval of the final version of work.

Natacha Sarmiento Rodríguez: Conception and design metodológico of investigation. Realization of active participation in the discussion of the results to be. Revision and approval of the final version of work.

Karel Yasmany Nápoles Florián: Conception and design methodological of investigation. Revision and approval of the final version of work.