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Sequential potentiometric determination of chloride and nitrate in meat products

R. Pérez-Olmos,[a]* R. Herrero,[a] J. L. F. C. Lima[b] & M. C. B. S. M. Montenegro[b]

[a]*Universidad del País Vasco, Departamento de Química Analítica, Escuela Universitaria de Ingeniería Técnica Industrial, Plaza de la Casilla 3, 48012, Bilbao, Spain*

[b]*Universidade do Porto, CEQUP, Departamento de Química–Física, Faculdade de Farmácia, Rua Anibal Cunha 164, 4000, Porto, Portugal*

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The analytical control of chloride and nitrate in meat products is important. For this reason in this work a sequential method for their determination by using chloride- and nitrate-selective electrodes has been developed. The extraction of both ions was carried out by stirring the samples for 30 min in a hot $5{\cdot}0\times10^{-2}$ mol litre^{-1} sulphuric acid solution. Direct potentiometry for chloride and multiple standard additions for nitrate were used as analytical techniques of measurement. The mean coefficient of variation and the average percentage of spike recoveries calculated for the chloride determination in five different meat products were 0·68% and 101%, respectively. For the nitrate determination these data were 0·84% and 101%, respectively. The limits of detection were 71·0 mg kg^{-1} and 23·2 mg kg^{-1} for chloride and nitrate, respectively. The mean chloride and nitrate concentrations determined by application of the developed method to 50 samples of meat products were found to be 21·1 g kg^{-1} and 133·5 mg kg^{-1}, respectively. Throughout the study, the Volhard titration for determination of chloride and the brucine spectrophotometric method for determination of nitrate, adopted as reference methods, were used simultaneously. Comparison of variances and linear regression analysis of the results obtained were carried out to validate the proposed sequential potentiometric method.

INTRODUCTION

Sodium chloride and sodium and potassium nitrate have been reported to have an antimicrobial action and are commonly used as preservatives in meat products. There are several reasons for limiting the amount of these compounds consumed by an individual. On the one hand, salt will have a direct impact on the health of many persons who have confirmed high blood pressure. On the other hand, nitrates, after prior reduction to nitrites, can react with amines to form toxic and carcinogenic nitrosamines.

Chloride in food is routinely determined by titration of solubilized chloride by the Volhard or Mohr methods. Because of the serious interference by other sample components, the ideal situation for the determination of chloride would be to isolate it from the interfering substances prior to its measurement. To accomplish this, ion-exchange chromatography and distillation methods have been suggested (Cerklewski & Ridlington, 1987). The use of chloride-selective electrodes in food analysis has been reviewed (Pérez-Olmos & Lima, 1989).

Many methods have been developed with the aim of determining nitrate in food. One of those most widely used is that based on the quantitative reduction of nitrate to nitrite using a cadmium column. The derivative formed after diazotization of sulphanilamide and coupling with naphthylethylenediamine is subsequently estimated spectrophotometrically (Frias *et al.*, 1992; Ruiz *et al.*, 1988). While this method is simple and easily carried out in a laboratory with few resources, it is inherently time-consuming. This makes difficult the routine analysis of large numbers of samples. The use of other instrumental analytical techniques such as fluorimetry, ion-selective electrodes and high-performance liquid chromatography has been proposed (Choi & Fung, 1980). Various liquid chromatographic procedures have been used because they are less time-consuming and the results highly reproducible (Alonso *et al.*, 1992; Dennis *et al.*, 1990; Sanderson *et al.*, 1991).

Spanish legislation (Ministerio de Sanidad y Consumo, 1985) recommends the Volhard method for the determination of chloride in meat products after hydroalcoholic extraction. This method is not entirely satisfactory because of the difficulty in visualizing the

*To whom correspondence should be addressed.

colour change of the indicator. Nitrate is extracted according to the same technique and determined by the brucine spectrophotometric method, but this procedure is handicapped by being time-consuming and lacking selectivity and reproducibility.

Since the properties and characteristics make ion-selective electrodes very attractive analytical tools, in this work a sequential method for the determination of chloride and nitrate in different meat products using chloride- and nitrate-selective electrodes has been developed. The limits of detection precision and accuracy have been established and the results obtained were compared with those obtained by simultaneous application of the official methods. In order to validate the proposed potentiometric method, statistical treatment of the data was carried out.

MATERIALS AND METHODS

Apparatus

The following equipment was used: a Perkin-Elmer Lambda 3B UV-V spectrophotometer, an Orion 710A digital pH/mV meter, an Orion 960 autochemistry system, an Orion 90-02 double-junction reference electrode, an Ingold 15 222 3000 nitrate-selective electrode, an Orion 91-02-SC pH electrode and a chloride-selective electrode constructed as previously described (Ferreira *et al.*, 1993).

Reagents

The chloride and nitrate stock solutions ($5{\cdot}0\times10^{-1}$ mol litre^{-1}) were prepared from solid sodium chloride and sodium nitrate previously dried at 110°C. The standard solutions used in the calibration curves and in the standard additions method were obtained by subsequent dilution of the stock solutions.

The outer chamber filling solution of the reference electrode ($1{\cdot}0\times10^{-1}$ mol l^{-1}) was prepared from solid ammonium sulphate and the inner chamber was filled with an Orion 90-00-02 reference electrode filling solution.

The interference suppressor solution was prepared by dissolving 16·7 g of $Al_2(SO_4)_3{\cdot}18H_2O$, 2·4 g of H_2NSO_3H and 1·4 g of H_3BO_3 in approximately 900 ml of deionized water. The pH of the solution was adjusted to 3·0–3·5 with a $1{\cdot}0\times10^{-1}$ mol litre^{-1} sodium hydroxide solution and finally diluted to 0·1 litre with deionized water. The ionic strength adjuster (ISA) solution (1·0 mol litre^{-1}) was prepared from solid ammonium sulphate.

Throughout the whole experimental work, distilled and deionized water with a conductivity of less than 0·1 μS cm^{-1} and analytical reagent grade chemicals were used.

Methods

Reference methods

Sample extraction Meat product (10 g), previously homogenized, was weighed into a 250 ml Erlenmeyer flask and 150 ml of ethyl alcohol (40%, v/v) were added. The solution was stirred and heated (80°C) for 1 h. After cooling, the solution was transferred to a 250 ml volumetric flask, 5·0 ml of each Carrez reagent were added and then diluted to volume with deionized water. Afterwards, the solution was mixed thoroughly, allowed to settle (10 min), centrifuged at 2000 rpm (5 min) and filtered through filter paper into a 200 ml volumetric flask. The solution was transferred to a 500 ml beaker and boiled to approximately 100 ml to drive out any remaining alcohol. After cooling, the solution was transferred again to a 200 ml volumetric flask and made up to volume with deionized water.

Chloride determination Extracted sample solution (10·0 ml) was pipetted to a 250 ml Erlenmeyer flask and 10·0 ml of 0·1 mol litre^{-1} standard silver nitrate solution, 1 ml of concentrated nitric acid, 1 ml of nitrobenzene and 50 ml of deionized water were added. The excess silver nitrate was titrated with a 0·1 mol litre^{-1} standard potassium thiocyanate solution using ferric alum as indicator.

Nitrate determination Extracted sample solution (10·0 ml) was pipetted into a 50 ml volumetric flask and 1·0 ml of chromogenic reagent (1·0 g of brucine and 0·1 g of sulphanilic acid dissolved in 100·0 ml of deionized water) and 10 ml of a 16 mol litre^{-1} sulphuric acid solution were added. After leaving for 10 min in the dark, 20 ml of deionized water were added, and, after shaking and leaving in the dark for another 15 min, the solution was cooled in an ice-bath to room temperature and made up to volume with deionized water. The absorbance of this solution (410 nm) was measured against a blank using a spectrophotometer. The nitrate concentration in the sample was determined by comparison with a calibration curve carried through the same experimental conditions.

Proposed method

Sample extraction Meat product (10 g), previously homogeneized, was weighed into a 250 ml Erlenmeyer flask and 65 ml of a sulphuric acid solution ($5{\cdot}0\times10^{-2}$ mol litre^{-1}) were added. The solution was stirred and heated (80°C) for 30 min. After cooling, the solution was transferred to a 100 ml volumetric flask, 5·0 ml of each Carrez reagent were added and the volume was completed with deionized water. Finally, the solution was shaken, allowed to settle and filtered through filter paper into a 100 ml beaker.

Sequential chloride and nitrate determinations Extracted sample solution (25·0 ml) was pipetted into a 100 ml beaker and 5·0 ml of an ISA solution were added. The chloride-selective and reference electrodes were immersed and the chloride concentration was determined by direct potentiometry.

After that, 10·0 ml of a $1{\cdot}6\times10^{-1}$ mol litre^{-1} silver sulphate–ammonium hydroxide solution were added and the solution filtered through filter paper into a 100 ml beaker. The pH of the filtrate, plus washing waters, was adjusted to 3·5–4·0 by adding a few drops of concentrated sulphuric acid. The solution was transferred to a 50 ml volumetric flask, 5·0 ml of the interference suppressor solution were added and the volume was completed with deionized water. This solution was poured out into a 100 ml beaker and the nitrate-selective electrode and the same reference electrode were immersed. The nitrate concentration was determined by application of the multiple standard additions method.

In order to establish the slopes of the electrodes in the same conditions as in the sample solution, a blank assay was carried out.

Assessment of the method The precision of the proposed potentiometric method was determined by its application to 11 samples of five different meat products and calculating the mean concentrations, the standard deviations and the coefficients of variation. After several additions of known concentrations of chloride and nitrate, the samples were analysed following the same method and the percentages of spike recovery determined were used to evaluate the accuracy.

The limit of detection was established according to the definition: 'limit of detection is the analyte concentration giving a signal equal to the mean signal of 11 blanks, plus three standard deviations of the blank' (Analytical Methods Committee, 1987).

In order to assess the quality of the results obtained by application of the developed analytical method, the samples were also analysed by the reference methods. A significance *F*-test (two-tailed test), at a 95% confidence level, was carried out to compare the standard deviations obtained by both methods. To compare the official and proposed extraction methods, 50 samples of meat products were simultaneously treated by both methods; the potentiometric procedure was applied and a linear regression analysis of the results obtained was carried out. The best fit equations, including the standard deviations of the slopes, the intercepts of the regression lines and their correlation coefficients, were calculated. A statistical test to see whether the correlation coefficients were indeed significant, at a 95% of confidence level and $n-2$ degrees of freedom, was also carried out (Miller & Miller, 1984).

RESULTS AND DISCUSSION

It is known that the brucine spectrophotometric method, recommended by the Spanish legislation (Ministerio de Sanidad y Consumo, 1985) for nitrate determination, presents poor reproducibility and accuracy. For this reason, the standard additions method, instead of the calibration curve, was adopted as the analytical technique of measurement. Since the paprika contained in many of the food products consumed in Spain introduces errors into the determination of the absorbance, it was necessary to add active carbon to the sample extracts before the analysis. The Volhard titration method, recommended for chloride determination, was applied without any modification.

The influence of ionic strength on potential values was studied, and the results showed that the addition of 5·0 ml of a 1·0 mol litre^{-1} ammonium sulphate solution (ISA) to 25·0 ml of the extracted sample was adequate for the potentiometric determinations of chloride and nitrate. Although the nitrate electrode is selective for nitrate, it also responds to other anions if significant amounts, relative to the nitrate concentration, are present. The most common interference is from chloride, which is present at high concentrations in meat products. In order to circumvent this problem, silver sulphate is added to the sample extract. Other ions, if present, also interfere; for this reason, an interference suppressor solution is needed. This solution also contains aluminium sulphate and sulphamic acid to remove carboxylic anions and nitrite, respectively. The interference of hydrogen carbonate is avoided if the solution is adjusted to pH 3·0–3·5. Since nitrate solutions are a culture medium for bacteria and algae, boric acid is also added to prevent biological growth if sample extracts need to be stored.

Different potentiometric techniques of measurement for the determination of chloride and nitrate in meat products were studied. For chloride determination, direct potentiometry, potentiometric titration and Volhard titration, adopted as the reference technique, were carried out. For nitrate determination, direct potentiometry, multiple standard additions and brucine spectrophotometry, as reference method, were studied. The precisions and accuracies of both determinations were calculated. From the data obtained it was possible to affirm that potentiometric titration, using the chloride-selective electrode as end-point detector and multiple standard additions, were the most precise and accurate potentiometric methods for the determination of chloride and nitrate, respectively.

The main problem associated with the potentiometric determination of nitrate is the presence of chloride, which was easily removed during its own determination, by precipitation, using a silver sulphate solution as titrant. However, in some samples it is possible to find high concentrations of chloride and low concentrations of nitrate. Consequently, during the determination of chloride, the volume of the titrant used increases, and after filtration the extract can not be made up to volume in the volumetric flask. In this case, the extract ought to be diluted but the nitrate concentration could be too low to be accurately determined with the nitrate-selective electrode.

In order to avoid this problem, a more concentrated titrant solution should be used, but unfortunately the titrant solution concentration is close to the solubility of

the silver sulphate. To increase this solubility it is necessary to dissolve the silver sulphate in ammonia (AOAC, 1984), but this means that the chloride concentration cannot be determined by potentiometric titration because of the presence of ammonia. Thus, the chloride concentration will be determined by direct potentiometry and then fixed volumes of silver sulphate, dissolved in ammonium hydroxide solution, and interference suppressor solution will be added prior to nitrate determination. The differences in terms of precision and accuracy between the direct potentiometry and the potentiometric titration methods are practically negligible and can be compensated by the greater rapidity of the procedure, which is important in routine analysis.

The values of precisions and accuracies obtained by application of the potentiometric techniques of measurement and by the reference procedures for the determination of chloride and nitrate in five different meat products after applying the official extraction method are shown in Tables 1 and 2.

To test whether the potentiometric and reference methods applied to the chloride and nitrate determinations differ in their precision, a significance F-test (two-tailed test) was carried out. In the chloride determination, the calculated F-values for all the products were less than the critical F-value, so there is no significant difference between the two standard deviations at the 95% confidence level. In the nitrate determination, the critical F-value was less than the calculated F-values, which confirms that there is a difference between both variances. If a one-tailed test for the nitrate determination is carried out, the calculated values exceed the critical F-value (2·98), which means that the proposed potentiometric method is more precise than the brucine spectrophotometric method adopted as reference technique (Miller & Miller, 1984).

From the data obtained for the chloride determination, it is possible to affirm that the mean concentrations obtained by the potentiometric method are in agreement with those supplied by the Volhard method. When the values of mean concentration for nitrate determination obtained using the proposed and reference methods were compared, a higher discrepancy was observed, as would be expected.

The official method of extraction is tedious and time-consuming. For this reason, a new extraction method has been developed. It is well known that the combination of

Table 1. Chloride (g kg^{-1}) in different meat products determined by direct potentiometry and Volhard titration, using the official extraction method

Meat product	Chloride determination							
	Direct potentiometry			Volhard titration			RE[d]	F-value
	x^a	CV[b]	R^c	x^a	CV[b]	R^c		
Salami	20·1 ± 0·2	0·8	101·3	19·9 ± 0·3	1·4	99·6	+0·9	2·62
Bacon	19·8 ± 0·2	1·1	101·5	19·2 ± 0·2	1·3	99·6	+3·4	1·28
Sausage	17·3 ± 0·1	0·8	101·8	17·1 ± 0·2	1·1	99·7	+1·5	1·80
Large sausage	15·5 ± 0·2	1·2	101·0	15·7 ± 0·2	1·6	99·7	−1·5	1·58
Hard pork sausage	11·4 ± 0·1	0·9	100·8	11·6 ± 0·2	1·4	99·5	−3·8	2·30

[a]Mean chloride concentration and standard deviation of 11 determinations.
[b]Coefficient of variation (%).
[c]Mean percentage of spike recovery (%).
[d]Relative error of the potentiometric method versus the reference method (%).
Critical F-value, considering a 95% of confidence level and 10 degrees of freedom, for a two-tailed test, is 3·72.

Table 2. Nitrate (mg kg^{-1}) in different meat products determined by multiple standard additions and UV spectrophotometry, using the official extraction method

Meat product	Nitrate determination							
	Multiple standard additions			UV spectrophotometry			RE[d]	F-value
	x^a	CV[b]	R^c	x^a	CV[b]	R^c		
Salami	63·2 ± 2·2	3·5	98·9	67·4 ± 8·5	12·7	88·5	−6·2	14·90
Bacon	163·6 ± 3·0	1·8	100·9	152·4 ± 13·2	8·7	94·7	+7·3	19·38
Sausage	89·5 ± 2·6	2·9	99·2	85·6 ± 8·7	10·2	91·3	+4·5	11·14
Large sausage	178·3 ± 2·7	1·5	99·5	170·8 ± 13·6	7·9	96·7	+4·4	25·41
Hard pork sausage	158·9 ± 3·9	2·4	100·7	168·1 ± 14·3	8·5	95·6	−5·5	13·70

[a]Mean nitrate concentration and standard deviation of 11 determinations.
[b]Coefficient of variation (%).
[c]Mean percentage of spike recovery (%).
[d]Relative error of the potentiometric method versus the reference method (%).
Critical F-value, considering a 95% of confidence level and 10 degrees of freedom, for a two-tailed test, is 3·72.

heat and low pH denature and precipitate the proteins and also liberate chloride and nitrate physically trapped by the sample matrix (Coveney, 1980). Since chloride and nitrate ions are being determined in the samples, only sulphuric acid can be used as extractant. In this study, samples were stirred and heated for different extraction times in sulphuric acid solutions whose concentrations ranged from $1{\cdot}0\times10^{-2}$ to 1·0 mol litre^{-1}. The official extraction method was also used for comparison. The chloride and nitrate contents were determined by the proposed potentiometric procedures. From the results obtained, it is possible to state that the best method for extracting chloride and nitrate in meat products is to add the sample to a $5{\cdot}0\times10^{-2}$ mol litre^{-1} sulphuric acid solution, which is then stirred and heated at 80°C. A plot of chloride and nitrate concentrations obtained from the acid extracts versus extraction times showed that 30 min were enough for complete extraction.

Samples of five different meat products have been simultaneously treated by the official and the developed extraction methods. Chloride and nitrate contents were sequentially determined in both extracts by the proposed potentiometric procedures, and the precisions and accuracies obtained in each case have been established.

The results summarized in Tables 3 and 4 showed that the precisions and accuracies obtained using the developed extraction method were similar to those supplied by the official extraction method. The same *F*-test, previously described, was carried out and the calculated *F*-values for the different meat products were less than the critical value, with the exception of salami for both determinations; thus there is no significant difference between the two standard deviations at the 95% confidence level.

The results obtained with the proposed extraction method for chloride and nitrate proved to be in agreement with those supplied by the official extraction method. The limits of detection of the two potentiometric determinations were found to be 71·0 mg kg^{-1} and 23·2 mg kg^{-1} for chloride and nitrate, respectively.

Fifty samples obtained from different types of Spanish meat products (ham, cured ham, smoked ham, bacon, salami, sausage, hard pork sausage, large sausage, bolognese sausage and chopped pork) were analysed in duplicate. After applying simultaneously both extraction methods and the proposed potentiometric procedures, the results showed that the chloride ranged from 12·6 g kg^{-1} (ham) to 45·1 g kg^{-1} (cured ham) with an

Table 3. Chloride (g kg^{-1}) in different meat products determined by direct potentiometry, using official and proposed extraction methods

Meat product	Chloride determination (direct potentiometry)							
	Proposed extraction			Official extraction			RE[d]	*F*-value
	x^a	CV[b]	R^c	x^a	CV[b]	R^c		
Salami	28·7 ± 0·1	0·1	100·7	28·0 ± 0·1	0·4	100·8	+2·3	5·00
Bacon	25·4 ± 0·2	0·8	99·6	24·7 ± 0·2	1·0	101·3	+2·8	1·55
Sausage	18·6 ± 0·2	0·9	100·9	18·3 ± 0·2	1·0	101·4	+1·5	1·10
Large sausage	22·6 ± 0·2	0·9	100·6	22·3 ± 0·2	1·0	101·2	+1·5	1·20
Hard pork sausage	23·2 ± 0·2	0·7	100·5	22·7 ± 0·2	0·9	100·8	+2·2	1·54

[a]Mean chloride concentration and standard deviation of 11 determinations.
[b]Coefficient of variation (%).
[c]Mean percentage of spike recovery (%).
[d]Relative error of the proposed extraction versus the official extraction (%).
Critical *F*-value, considering a 95% of confidence level and 10 degrees of freedom, for a two-tailed test, is 3·72.

Table 4. Nitrate (mg kg^{-1}) in different meat products determined by multiple standard additions, using official and proposed extraction methods

Meat product	Nitrate determination (multiple standard additions)							
	Proposed extraction			Official extraction			RE[d]	*F*-value
	x^a	CV[b]	R^c	x^a	CV[b]	R^c		
Salami	202·0 ± 0·5	0·2	100·6	204·1 ± 1·5	0·8	99·1	−1·0	10·42
Bacon	158·8 ± 1·5	0·9	100·2	158·3 ± 2·3	1·5	101·0	+0·3	2·41
Sausage	91·5 ± 0·7	0·8	100·6	90·6 ± 1·2	1·3	99·4	+0·1	2·23
Large sausage	188·3 ± 1·6	0·8	100·1	190·1 ± 2·5	1·3	99·8	−0·9	2·48
Hard pork sausage	177·1 ± 2·5	1·4	100·3	180·5 ± 3·7	2·1	100·8	−1·9	2·16

[a]Mean nitrate concentration and standard deviation of 11 determinations.
[b]Coefficient of variation (%).
[c]Mean percentage spike recovery (%).
[d]Relative error of the proposed extraction versus the official extraction (%).
Critical *F*-value, considering a 95% of confidence level and 10 degrees of freedom, for a two-tailed test, is 3·72.

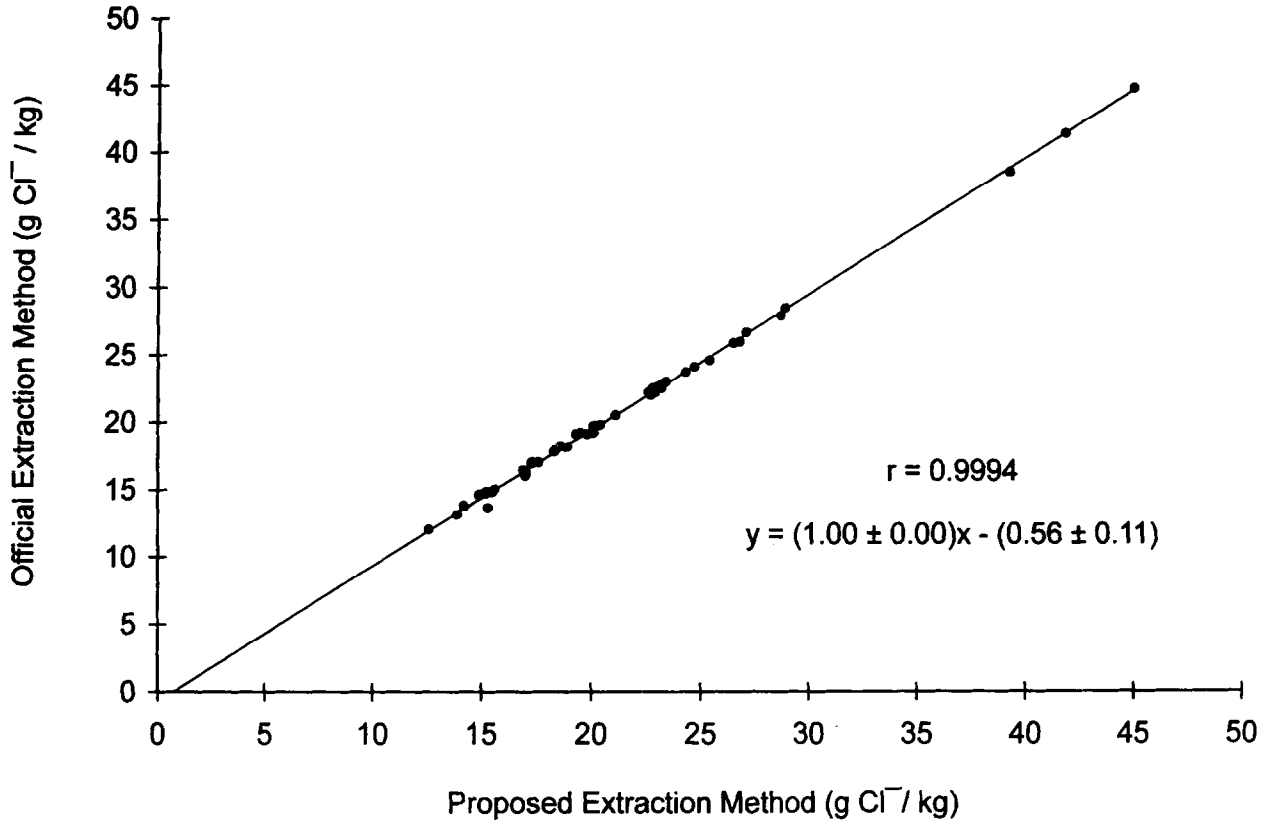

Fig. 1. Regression analysis, for the chloride determination, comparing the results obtained by the potentiometric methods applying the proposed and official extraction methods.

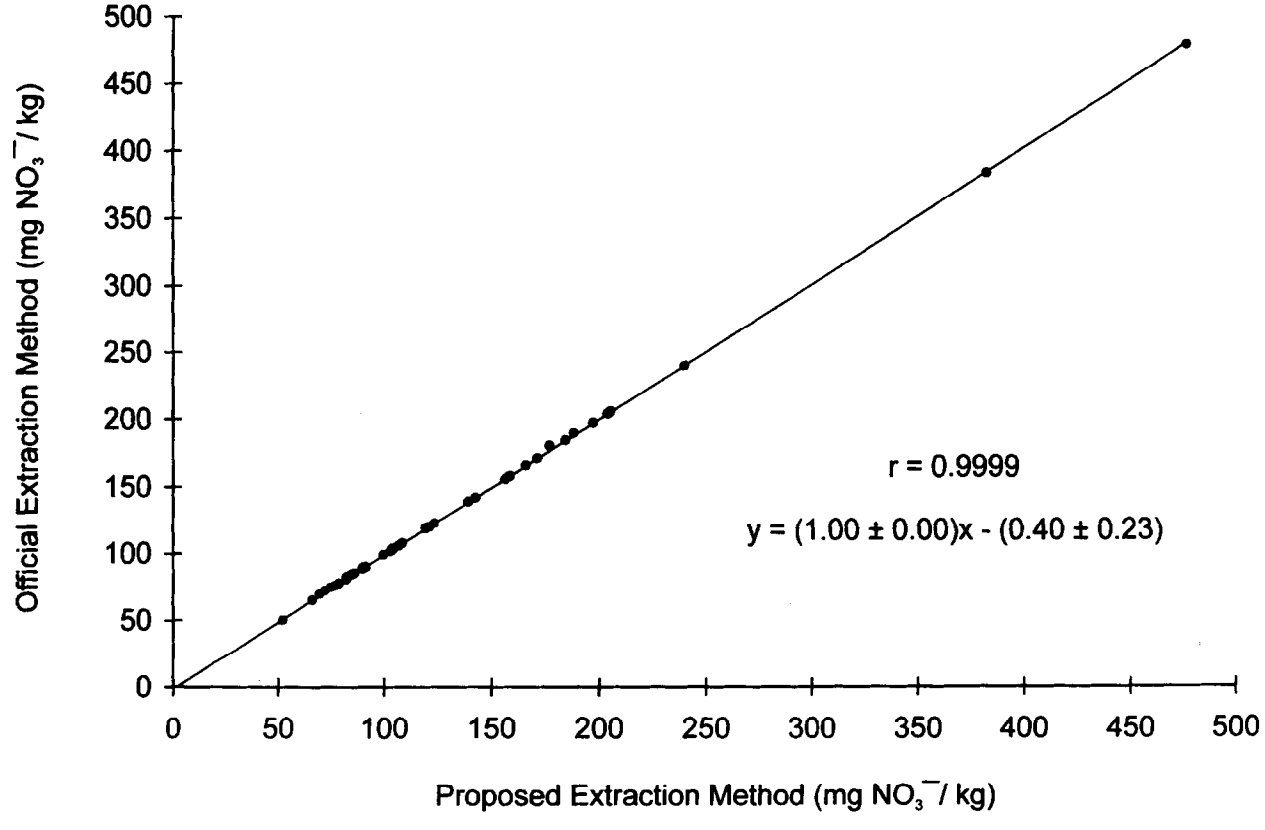

Fig. 2. Regression analysis, for the nitrate determination, comparing the results obtained by the potentiometric methods applying the proposed and official extraction methods.

average value of 21·1 g kg^{-1}. Although three samples showed higher values, it is possible to state that there was no dispersion of the results obtained since 94·0% of the samples were in the range 10·0–30·0 mg kg^{-1}. The nitrate concentration ranged from 52·1 mg kg^{-1} (chopped pork) to 478·5 mg kg^{-1} (hard pork sausage), with an average value of 133·5 mg kg^{-1} and a larger distribution than for chloride determinations. Only seven samples showed abnormally high values and 86·0% of the samples were included in the concentration range 50·0–200·0 mg kg^{-1}.

The data calculated by linear regression analysis of the results are shown in Figs 1 and 2. The confidence limits of the slopes and intercepts of the regression lines, at a 95% confidence level and $n-2$ degrees of freedom, were also calculated (Miller & Miller, 1984). The values were $b = 1 \cdot 00 \pm 0 \cdot 01$ and $a = 0 \cdot 56 \pm 0 \cdot 23$ for the chloride determination, and $b = 1 \cdot 00 \pm 0 \cdot 00$ and $a = 0 \cdot 40 \pm 0 \cdot 47$ for the nitrate determination. From these data it is possible to affirm that, in the case of nitrate determination, the calculated slope and intercept do not differ significantly from the ideal values of 1 and 0, respectively, and thus that there is no evidence for systematic differences between the two extraction methods. In the chloride determination there is no deviation from the ideal value of the slope, but a non-zero intercept was obtained and a very slight tendency to get higher values with the proposed extraction method than with the official extraction method was observed. However, this difference it is not too significant taking into account the high chloride concentrations usually found in these types of meat products.

Finally, a statistical test to see whether the correlation coefficients are indeed significant were applied. From the correlation coefficients, the t-values were calculated at a 95% of confidence level and $n-2$ degrees of freedom; the results obtained were $t = 200 \cdot 16$ and $t = 692 \cdot 57$ for the chloride and nitrate determinations, respectively. These values are greater than the tabulated t-value (2·26), so it is possible to state that significant correlations exist between both extraction methods.

CONCLUSIONS

From the perspective of food control, the application of this new extraction method followed by the use of chloride- and nitrate-selective electrodes may be considered an advantageous alternative to determine these ions in meat products. The sequential recommended potentiometric procedure developed is rapid, simple to operate, requires inexpensive equipment and its precision and accuracy are similar to those of the reference method for chloride determination, and better for nitrate determination.

The data obtained in this work relative to the chloride and nitrate contained in Spanish meat products were in accordance with those reported previously using volumetric methods for the determination of chloride (García *et al.*, 1982) and spectrophotometric methods for the determination of nitrate (Frias *et al.*, 1992; Gutiérrez *et al.*, 1994).

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