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Determination of Halides in Wines by Ion-Selective Electrodes

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ABSTRACT

An ion-selective electrode procedure is used for the determination of fluoride, chloride, bromide and iodide in 51 red and rosé wines from DOC areas of Southern Italy.

Fluoride and iodide are present at levels lower than 1 mg/litre, with average values of 0·32 and 0·023 mg/litre, respectively.

Chloride is present at concentrations varying from 21·9 to 99·2 mg/litre, not exceeding, therefore, the limits set by the Italian law.

The average value of bromide is 0·78 mg/litre, but three samples are found to exceed the international limit (1·0 mg/litre) set for wines.

INTRODUCTION

Halides are usually present in wine; however, in some instances a substantial increase with respect to the natural content can be observed. Anomalous levels might derive mainly by the use of antiseptics, disinfectants (Amerine, 1958; Gandini, 1969; Cava & Cavallaro, 1979; Vecchio *et al.*, 1981) or because of particular local pollution problems (Mammi *et al.*, 1976; Vecchio *et al.*, 1981).

As a consequence of the considerable implications, from both health and

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legal viewpoints, it is relevant to determine the contents of such elements both in wines (Florentin & Navellier, 1951; Mecca, 1952; Amerine, 1958; Jaulmes *et al.*, 1962; Eschnauer, 1967; Amerine & Ough, 1974; Graf *et al.*, 1976; Mammi *et al.*, 1976; Cava *et al.*, 1979; Vecchio *et al.*, 1981; Garoglio, 1981; Bernal *et al.*, 1983) and in other foods (Ferren & Shane, 1969; Muldoon & Liska, 1971; Randell & Linklater, 1972; De Clercq *et al.*, 1974; Altinata *et al.*, 1978; Bruhn & Franke, 1978; Miles, 1978; Lacroix & Wong, 1980).

Numerous methods have been used in the past to ascertain the content of the halides in wine. These are colorimetric (Jaulmes *et al.*, 1962; Amerine *et al.*, 1974; Mammi *et al.* 1976), chemical (Amerine, 1958; Amerine *et al.*, 1974), and biochemical (Mecca, 1952) methods, which involve a different pretreatment of the sample for each halide analysis. However, these classical techniques are considered tedious and expensive to use as routine analytical tools in a winery laboratory.

The advent of practical ion-selective electrodes has generated much interest among analytical chemists for its application in a wide variety of matrices such as milk (Muldoon & Liska, 1971; De Clercq *et al.*, 1974; Bruhn & Franke, 1978; Sekerka & Lechner, 1978; Lacroix & Wong, 1980), drinking water (Altinata *et al.*, 1978), nutritional beverage products (Ferren & Shane, 1969; Miles, 1978; Sekerka & Lechner, 1978), cheese (Randell & Linklater, 1972), soil (Larsen & Widdowson, 1971; Sekerka & Lechner, 1978), biological samples (Stahr *et al.*, 1971; Sekerka & Lechner, 1978), vegetable oils (Conacher & McKenzie, 1977), waste water (Sekerka & Lechner, 1978) and wines (Graf *et al.*, 1976; Cava & Cavallaro, 1979; Vecchio *et al.*, 1981; Bernal *et al.*, 1983). The widespread use of ion-selective electrodes has been favoured because of their speed and ease of use.

In the present study we have applied this technique to the determination of F^-, Cl^-, Br^- and I^- in red and rosé wines from DOC areas of Southern Italy. Each wine represents a single vine and the different environmental conditions in which it grows.

METHOD

Technique

The halide ion electrodes used are solid-state electrochemical sensors designed to determine the activity of free halide ions and, consequently, their concentration.

Each element is determined by the specific ion-selective electrode coupled with a suitable reference electrode. When operating with a chloride ion electrode in samples more diluted than 10^{-3} M, the reference electrode is placed in salt bridge solution to prevent chloride ion contamination. Each electrode, with the exception of F^-, is filled with a reference solution, having a fixed silver ion concentration (10^{-2} M $AgNO_3$), with polycrystalline pellets of Ag_2S mixed with the corresponding silver halides as the active phase.

The fluoride-sensitive electrode, due to its outstanding selectivity, is constructed with an internal solution 0·1 M in both sodium chloride and sodium fluoride. Here the sensing element between the internal solution and the solution under test consists of a LaF_3 single crystal doped with Eu^{+2}.

In all the electrodes a voltage is developed across the membrane, which depends on the relative ion activity in the solution in which the electrode is immersed, according to the well-known Nernst equation. The practical concentration limits of detection for F^-, Cl^-, Br^- and I^- electrodes, as given by the manufacturer, are: 1×10^{-6}; $1{\cdot}3 \times 10^{-5}$; $8{\cdot}8 \times 10^{-7}$ and $1{\cdot}2 \times 10^{-8}$ M, respectively.

Operating conditions

To analyze the wine samples, we used the standard addition method (Beckman Instr. 015-555570; Beckman Instr. 015-556313; Cammann, 1979) that offers the advantages of rapidity, simplicity and increased accuracy, when taking into account the complexity of the matrix and the low content of the sought-after ions.

Slope was determined by two addition measurements, the first of 1 ml and the second of 10 ml of standard solution in a blank matrix solution containing 12% of ethanol and 10% of ISAB solution, for the slope of Cl^-, Br^- and I^-, and 10% of TISAB solution, for that of F^-. During slope checks, and ion determination in samples, we always employed the same hydrodynamic conditions and temperature. As explained in the following 'Procedure' section, we preliminarily added to the sample solutions, for Cl^-, Br^- and I^-, an ISAB solution containing:

(a) An inert electrolyte, in order to operate at constant ionic strength.
(b) A suitable buffer system stabilizing pH in the range of 4 to 5.

For F^-, on the other hand, a TISAB solution was added that buffered the pH between 5·0 and 5·5, to avoid hydroxide interferences or the formation of hydrogen complexes of fluoride.

The sensing membrane of solid-state electrodes may become inactive or contaminated with use, due to some substances present in wine. In this case, the electrode response will appear slow, drift, or exhibit poor slopes and reproducibility. To restore performance the electrode membrane should then be polished to a mirror-like finish, using a polishing disk moistened with deionized water.

Reagents and apparatus

For all solutions, deionized double distilled water was used. Other reagents and conditions were as follows:

(a) Reagents of analytical grade, dried at 105°C, were used to prepare standard solutions.
(b) To adjust the pH and the ionic strength, and to prevent complexing of fluoride, TISAB solution (containing 57 ml of CH_3COOH, 58 g of NaCl and 4 g of CDTA) was used, while ISAB solution (containing $NaNO_3$ 5M, CH_3COOH and NaOH) was used for the other halides.
(c) Electrodes: the six electrodes were supplied by Beckman Analytical srl.
(d) pH meter: digital, selectIon™ 5000 Beckman ion analyzer.
(e) Magnetic stirrer: with teflon-coated stirring bar. A foam pad was placed on top of the magnetic stirrer to reduce heating effects from the stirrer motor.
(f) As for the samples examined, we analyzed 51 wines representative of the different cultivars of Southern Italy. The red wines were made from cv. Primitivo, Uva di Troia, Negro Amaro and Aglianico del Vulture; the rosé wines only from cv. Negro Amaro.

Procedure

50 ml of wine were transferred into a 250-ml beaker, and 5 ml of ISAB (for Cl^-, Br^- and I^-) or TISAB (for F^-) solution were added. After 5 min the electrodes were immersed, and the instrumentation standardized by applying the concentration determination method, employing a standard addition with a known electrode slope (Beckman Instr. 015-555570; Beckman Instr. 015-556313; Cammann, 1979). After standardization, 1·0 ml of standard ion solution (about one hundred times more concentrated than expected sample concentration) was added and the concentration was determined.

RESULTS AND DISCUSSION

The results of the analyses of 51 wine samples are summarized in Table 1, presenting the minimum, average and maximum values for each different type of wine. Overall values are given as last entries.

In Table 2 the degrees of freedom (df) and the mean square, both between various types of wine and within types of wine, are reported for each element.

TABLE 1

Minimum, Mean and Maximum Halide Contents of each Type of Wine and of all Samples Taken Together (All Values in mg/litre)

Wines		*F⁻*	*Cl⁻*	*Br⁻*	*I⁻*
	min.	0·18	32·9	0·59	0·014
Primitivo	av.	0·27	54·5	0·75	0·022
(13 samples)	max.	0·44	99·2	0·88	0·027
	min.	0·18	21·9	0·69	0·011
Uva di Troia	av.	0·32	52·0	0·93	0·022
(9 samples)	max.	0·52	91·4	1·44	0·031
	min.	0·28	35·6	0·77	0·012
Negro Amaro (rosé)	av.	0·33	54·7	0·85	0·024
(8 samples)	max.	0·42	66·2	0·91	0·045
	min.	0·30	28·4	0·61	0·018
Negro Amaro (red)	av.	0·35	52·1	0·75	0·029
(11 samples)	max.	0·42	66·2	0·89	0·041
	min.	0·28	25·5	0·59	0·012
Aglianico del Vulture	av.	0·35	36·0	0·67	0·020
(10 samples)	max.	0·50	50·0	0·75	0·030
	min.	0·18	21·9	0·59	0·011
Overall	av.	0·32	50·0	0·78	0·023
(51 samples)	max.	0·52	99·2	1·44	0·045

The accuracy of data for each element was estimated by determining the recovery of added halides by the procedure proposed. For each element the error limit was always less than ±2%.

The precision, measured as RSD, when the halide ion concentration in the same sample was repeatedly determined by the proposed technique, was: 2·08; 0·39; 3·91 and 10·13% for F^-, Cl^-, Br^- and I^-, respectively.

Inspection of the data presented in Table 1 allows one to note the following relevant points.

TABLE 2

The Main Data from the Analysis of the Mean Square

Source of variance	*df*	*Mean square*			
		F⁻	*Cl⁻*	*Br⁻*	*I⁻*
Between types of wine	4	$1{\cdot}36 \times 10^{-2}$	622·3	$9{\cdot}67 \times 10^{-2}$[a]	$1{\cdot}16 \times 10^{-4}$
Within types of wine	46	$0{\cdot}68 \times 10^{-2}$	260·1	$1{\cdot}74 \times 10^{-2}$	$0{\cdot}53 \times 10^{-4}$

[a] Extremely significant differences between the average values of various types of wine.

Fluoride

Small amounts of fluoride are present normally in musts and wines. Abnormally high concentrations of this element might result from the use of fluorides and fluorosilicate as an antiseptic, or from employing, in winemaking, grapes sprayed with fluoride-containing compounds, or grown in areas polluted by chemical industries (Mammi *et al.*, 1976). Widespread fluoride in the environment, as well as in food and drinks, however, causes, considerable concern. Constant, prolonged exposure to high levels of fluoride can, in fact, cause typical ailments of the skeleton (Mammi *et al.*, 1976).

The levels of total fluoride found in our study are rather low, i.e. from 0·18 to 0·52 mg/litre, with an average value of 0·32 mg/litre. In 92% of the samples (Fig. 1) fluoride does not exceed 0·44 mg/litre, while, in just two samples, from the same area, it exceeds the concentration of 0·50 mg/litre. This is considered the limit value for wines by the standards of some European nations.

On average, wines made from the Primitivo cultivar show a lower fluoride concentration (av. 0·27 mg/litre) than that observed in other cultivars. However, statistical analysis of these values does not show any important differences (Table 2).

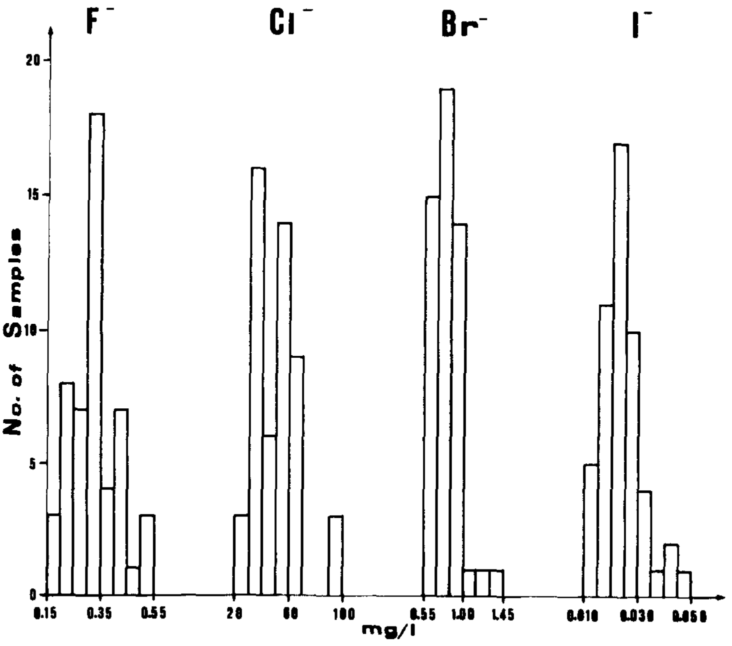

Fig. 1. Frequency intervals of the amounts (mg/litre) of halides in 51 wine samples.

The literature is rich in reports on the determination of fluoride in wines. Many papers indicate values around a fraction of 1 mg/litre, as reported, for example, in the reviews by Amerine (Amerine, 1958) and Vecchio (Vecchio *et al.*, 1981). Much higher levels (up to 28 mg/litre) are sometimes reported (Amerine, 1958; Mammi *et al.*, 1976; Vecchio *et al.*, 1981) and are attributed to special treatments and/or to the presence of specific sources of pollution near the wineyards.

Chloride

The current Italian legislation establishes that Cl^- (as NaCl) in wines should be less than 0·5 g/litre (Vitagliano, 1982). Usually, wines contain amounts of Cl^- lower than 0·1 g/litre. Larger quantities can be found in wines made from grapes irrigated with high-salt water, or cultivated in areas nearby the sea, where they experience the effect of the salt blown in by the wind. Winery practices, such as the use of anion-exchange for tartrate stabilization, the illegal use of monochloroacetic acid as an antiseptic and the use of gelatine for the process of clarifying the wine (Amerine, 1958; Amerine & Ough, 1974; Vitagliano, 1982; Bernal *et al.*, 1983), can affect the Cl^- content quite considerably.

In our wine samples, chlorides are present in low concentrations, between 21·9 and 99·2 mg/litre, with an average value of 50·0 mg/litre, never exceeding, however, 0·10 g/litre of Cl^-, which is considered the normal limit. As can be seen from Fig. 1, only three samples exceed the value of 90 mg/litre (as Cl^-), while 94% contain less than 70 mg/litre. Wines which are made from the Aglianico del Vulture cultivar have lower quantities of Cl^- (average, 36·0 mg/litre). In spite of this, there are no significant effects on the analysis of the mean square. Its value does not show, at a probability level of 0·05, any significant influence of the type of wine.

Concentration intervals similar to those observed by us are reported in Amerine's vast review (Amerine, 1958) for both Italian and foreign wines, whilst values even higher than 0·5 g/litre (expressed as NaCl) have been determined by some authors in non-Italian wines.

Bromide

The international limit set for Br^- in wines is 1 mg/litre. Normally, the content of bromide in grapes and wines is quite low (< 1 mg/litre). Even wines obtained from vineyards nearby the sea, which seems to contribute to the levels of both Br^- and Cl^-, never contain more than 1 mg/litre of bromide (Florentin & Navellier, 1951). Concentrations over this limit can be due to the addition of organic bromine-containing antiseptics, such as monobromoacetic acid and its esters (now illegal). Also the use, in the vineyards, of bromine-containing fungicides, insecticides and disinfectants from the tanks or other vinery equipment, can be the cause of an anomalous increase in Br^- concentration (Amerine, 1958).

In this study, the observed range of Br^- concentration was from 0·59 to 1·44 mg/litre with an average value of 0·78 mg/litre. However, for 94% of the samples, the Br^- concentration was spread over a narrower range (Fig. 1). Of over 51 samples of wine analyzed, only three, which came from vineyards near the sea, exceeded the legal limit set for Br^-, and in two of them, the content of Cl^- was also relatively high.

This trend was emphasized by the analysis of variance (Table 2). This reveals significant differences between the average values of the different types of wine, which is probably due to the different environmental conditions in which the various wines are normally cultivated. In fact, the Aglianico del Vulture cultivar is the only one which grows in inland areas and therefore is not affected in any way by the sea. Hence, the average value of Cl^- for this wine (36·0 mg/litre), is the lowest of the average values.

Inspection of the literature data, however, reveals that, in the presence of a bromide ion contamination factor, the legal limit is greatly exceeded (3 mg/litre and 7·5 mg/litre) (Amerine, 1958), (5·5 mg/litre and >20 mg/litre) (Graf *et al.*, 1976).

In any case, the Br^- concentration range that we observed is in line with the values reported by Graf (Graf *et al.*, 1976) for bromide ion content in various European wines.

Iodide

The few available data in the literature concerning the levels of I^- in wines demonstrate that this element is normally present at very low concentrations. Generally, authors employing different techniques for determining I^- in wines rarely found it in amounts exceeding 0·6 mg/litre (Amerine, 1958; Eschnauer, 1967; Cava & Cavallaro, 1979; Garoglio, 1981; Vecchio *et al.*, 1981). Higher levels can be verified in wines to which organic antifermentatives have been added, or when substances containing iodide have been used during the cleaning and disinfection of the winery containers and instruments (Gandini, 1969; Cava & Cavallaro, 1979).

The concentrations of I^- ascertained in this work were between 0·011 and 0·045 mg/litre (average value, 0·023 mg/litre), which are among the lowest values recorded in the literature. These values compare well with those reported by Follemberg and Mayerhofer (Amerine, 1958; Cava & Cavallaro, 1979; Vecchio *et al.*, 1981).

When comparing the average values (Table 1) of the various cultivars, it is hard to see any substantial difference. Even when the variance value (Table 2) is analyzed no significant differences between the averages can be seen. This in itself confirms the view that there is no correlation between soil conditions and iodide content (Amerine, 1958).

Unfortunately, the repeatability of data for this element (10·13%), measured as RSD, is far from satisfactory. This can be attributed to the extremely low iodide concentrations in the samples examined in this study (average value, 0·023 mg/litre).

CONCLUSIONS

The procedure proposed in the present study proves to be rapid, simple and reliable. The use of samples which have not been pre-treated prevents the loss of halides during the preparatory step.

The determinations have a good accuracy. The level of error, in fact, for each element is always less than ±2%. The precision is 2·08, 0·39, 3·91 and 10·13% (values of RSD) for F^-, Cl^-, Br^- and I^-, respectively. These values are acceptable even for I^-, whose average value in our samples was found to be 0·023 mg/litre. For the other elements the respective average values were 0·32, 50·0 and 0·78 mg/litre.

The variance analysis does not reveal, for F^-, Cl^- and I^-, any significant differences between the average values of the various types of wine. In the case of Br^-, the influence of the cultivar, at a probability level of 0·01, is very significant.

REFERENCES

Altinata, A., Pekin, B. & Ülgü, S. (1978). Determination of iodine using a kinetic method with an iodide ion-selective electrode. *Analyst*, **103**, 876.

Amerine, M. A. (1958). *Advances in food research*. Vol. 8. Mrak, E. M. & Stewart, G. F. (Eds), Academic Press, New York, 142.

Amerine, M. A. & Ough, C. S. (1974). *Wine and must analysis*. J. Wiley & Sons, New York, 99.

Bernal, J. L., Del Nozal, J., Aller, A. J. & Deban, L. (1983). Nota. Determinaciòn de cloruro en vinos con un electrodo selectivo. *Tecnol. Aliment.*, **23**(1), 137.

Bruhn, J. C. & Franke, A. A. (1978). An indirect method for the estimation of the iodine content in raw milk. *J. Dairy Sci.*, **61**, 1557.

Cammann, K. (1979). *Working with ion-selective electrodes*. Springer-Verlag, Berlin, Heidelberg, New York, 137.

Cava, L. & Cavallaro, A. (1979). Valutazione del contenuto di iodio nei vini. *Boll. Chim. Un. It. Lab. Prov.*, **30**, 140.

Conacher, H. B. S. & McKenzie, A. D. (1977). Food additives. Comparison of iodometric titration, potentiometric titration, and bromide ion electrode determination for bromide in brominated vegetable oils. *J. Assoc. Off. Anal. Chem.*, **60**(4), 918.

De Clercq, H. L., Mertens, J. & Massart, D. L. (1974). Analysis of chloride in milk with a specific ion electrode. *J. Agr. Food Chem.*, **22**(1), 153.

Eschnauer, H. (1967). Über spurenelemente im wein. *Z. Lebensm. Unters. Forsch.*, **134**, 13.

Ferren, W. P. & Shane, N. A. (1969). Potentiometric determination of fluoride in beverages by means of the ion selective solid state electrode. *J. Food Sci.*, **34**, 317.

Florentin, D. & Navellier, P. (1951). Sur la teneur en brome normal des vins naturels francais. *Ann. Fals. Fraud.*, **44**, 297.

Gandini, A. (1969). Indagini microbiologiche sul moscato d'Asti. Nota III. L'inquinamento microbico dell'Asti Spumante nel corso dell'imbottigliamento ed effetto dell'impiego di uno iodoforo. *Vini d'Italia*, **63**, 527.

Garoglio, P. G. (1981). *Nuovo Enologia. Edizioni AEB Brescia*, 292.

Graf, J. E., Vaughn, T. E. & Kipp, W. H. (1976). Analysis of bromide ion in wine by ion selective electrode. *J. Assoc. Off. Anal. Chem.*, **59**(1), 53.

Jaulmes, P., Brun, S. & Cabanis, J. C. (1962). Chloride and bromide content of wine and the investigation of brominated antiseptics. *Chim. Anal.*, **44**, 327.

Lacroix, D. E. & Wong, N. P. (1980). Determination of iodide in milk using the iodide specific ion electrode and its application to market milk samples. *Journal of Food Protection*, **43**(9), 672.

Larsen, S. & Widdowson, A. E. (1971). Soil fluorine. *J. Soil Sci.*, **22**(2), 210.

Mammi, F., Manfredini, M. & Tognoni, E. (1976). Indagine sul contenuto in piombo e in fluoro di alcuni prodotti agrari di un comprensorio ceramico. *Boll. Chim. Un. It. Lab. Prov.*, **27**, 190.

Mecca, F. (1952). Un metodo di determinazione biochimico dei fluori nei vini. *Chim. e Ind.*, **34**, 345, 568.

Miles, P. (1978). Vitamins and other nutrients. Determination of iodide in nutritional beverage products using an ion selective electrode. *J. Assoc. Off. Anal. Chem.*, **61**(6), 1366.

Muldoon, P. J. & Liska, B. J. (1971). Chloride ion activity electrode for the detection of abnormal milk. *J. Dairy Sci.*, **54**, 117.

Randell, A. W. & Linklater, P. M. (1972). The rapid analysis of cheddar cheese. I. The determination of salt content using an electrode specific for chloride ion. *J. of Dairy Technology*, 51.

Sekerka, I. & Lechner, J. S. (1978). Metals and other elements. Ion selective electrode for determination of chloride ion in biological materials, food products, soil, and waste water. *J. Assoc. Off. Anal. Chem.*, **61**(6), 1493.

SelectIon ^{TM}5000 Ion Analyzer-Beckman Instructions 015-555570; Fullerton, CA 92634, August, 1979, 780663, Printed in USA.

SelectIon ^{TM}5000 Ion Analyzer-Beckman Instructions 015-556313; Fullerton, CA 92634, February, 1980, 791803, Printed in USA.

Stahr, H. M., Clardy, D. O. & Buck, W. B. (1971). Screening test for fluoroacetate in baits and biological samples. *J. Assoc. Off. Anal. Chem.*, **54**(5), 1235.

Vecchio, A., Finoli, C., Germani, S. & Cerutti, G. (1981). Vini genuini italiani. Nota 3. Iodio e fluoro. *Tecnologie Alimentari*, **5**, 10.

Vitagliano, M. (1982). *Industrie Agrarie*. UTET Torino.