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Comparative Study of Ion-Selective Electrodes Versus Flame Emission Photometry Techniques for the Determination of Sodium and Potassium in Spanish Wines

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ABSTRACT

The behaviour of sodium and potassium selective electrodes is described, using two analytical methods to determine the concentrations of both ions in sixty-three samples of red, rosé and white wines, taken from several wine growing areas in Spain. The analytical measurement technique adopted has been Multiple Known Addition, and the equipment used for this purpose has been the Autochemistry System Orion 960. Precision and accuracy of the recommended procedures, expressed in terms of the standard deviation and percentage of spike-recovery, are good and the results show a great concordance with those obtained by flame emission photometry, the reference technique.

INTRODUCTION

The amount of potassium in unfermented grape juice depends on a great number of variables, such as properties of the soil, climatic factors, time and temperature of both fermentation and storage process, use of ion-exchange resins, presence of compounds employed as aids in filtration operations, etc. (Amerine & Ough, 1980). The determination of potassium and tartrates contents in wine is important since high potassium levels will cause harmless, although unaesthetic, precipitates in bottled wine. The sodium content also depends on the same factors and is usually very low, with the exception of musts from wine growing areas localized near the sea. The sodium content in

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wine is regulated in some countries because it will have a direct impact on the health of many persons who have confirmed or borderline high blood pressure. In addition to the classical methods of chemical quantitative analysis, the instrumental techniques recommended for the determination of sodium and potassium contents in wine are atomic absorption spectrometry and flame emission photometry. This paper describes a potentiometric determination of both ions in wine, using sodium and potassium selective electrodes. The behaviour of the electrodes has been studied in terms of sensibility, time-response, influence of percentage of alcohol, pH, ionic strength and interferences. Multiple Known Addition was chosen as the optimum analytical technique of measurement, since we have been using it in our laboratory for years with excellent results. In this well-known potentiometric method of measurement the sample concentration is obtained by extrapolation of the line drawn when plotting potential values versus added volumes of the standard solution on semi-antilogarithmic paper, designed by Gran. Although in batch analysis the method can be time-consuming, it gives adequate precision and accuracy.

Among eleven other methods of measurement the computerized Autochemistry System, Orion 960, has a built-in program which makes it possible to carry out this multiple increment method in a simple and quick way. A measured volume of wine sample is placed in a beaker and measured volumes of ionic strength adjustor (ISA) and diluent are added, so the final volume before starting the additions will be known. The equipment adds standard solution of the analyzed ion from a volumetric pump based on a rotary reciprocating piston. When a stable value of potential has been achieved, it is recorded according to a stability criterion preselected by the analyst when programming. Having made several additions of standard solution, there is enough data to calculate how well each point of the successive additions conforms to the theoretical relationship embodied in the Nernst equation. The analysis is stopped when the precision of the fit of the observed data is better than some value preselected by the analyst (Comer & Avdeef, 1987). Since there are more experimental data than the numbers of parameters to be determined, the equipment is able to calculate two important statistical parameters. One is the precision of the fit previously mentioned, expressed in terms of standard deviation, and the other is the spike-recovery. If there exists a matrix effect that gives a large recovery error, this appears printed alongside the results given by the equipment. In this way, it is possible to affirm that the technique audits itself.

The precision and accuracy of the analytical procedures recommended have been established. Finally, sixty-three samples of red, rosé and white wines, from different wine growing areas in Spain, were analyzed by application of the analytical procedures proposed in this paper, and simultaneously, by flame emission photometry, the reference technique. The results that were obtained were compared by means of linear regression analysis.

MATERIALS AND METHODS

Apparatus

An Orion 960 Autochemistry System, an Orion model 93–19 potassium selective electrode, an Orion model 97–11 sodium selective electrode, an Orion model 90–02 double junction reference electrode and a Dr Bruno Lange Flame Photometer, model M6a, were used.

Reagents

Working sodium standard solution: 10^{-2}M sodium chloride solution. Working potassium standard solution: 4×10^{-2}M potassium chloride solution. Sodium ionic strength adjustor: 20% v/v triethanolamine solution. Potassium ionic strength adjustor: 5M sodium chloride solution. Electrode reference filling solutions: Inner solution for both determinations, the same as shipped with the reference electrode. Outer solution for potassium analysis prepared by dilution of 2 ml of ISA solution to 100 ml in a volumetric flask. Outer solution for sodium analysis prepared by weighing 0·5 g of ammonium chloride and dissolving in 100 ml of de-ionized water.

All chemicals used were Merck analytical-reagent grade or similar. Distilled de-ionized water was used throughout.

Behaviour of the electrodes

As in the recommended procedures, samples of wine were diluted in a ratio 1:10. Assuming that the average percentage of alcohol in wine is 10% v/v, the concentration of alcohol in wine samples before being analyzed is approximately 1% v/v. For that reason, calibration curves for sodium and potassium with 1% of ethanol content were performed. There was no significant deviation of the potential values if compared with those obtained in an aqueous medium.

The detection limit, defined as the concentration of sodium or potassium at which the electrode potential deviates by 18 mV/n_i from the extrapolated linear portion of the calibration graph, was found to be 0·13 mg dm^{-3} for the sodium electrode and 0·29 mg dm^{-3} for the potassium electrode. These data were obtained from eleven daily calibration curves with 1% ethanol.

The response time of both electrodes was obtained from plots of potential values versus time for aqueous and 1% ethanolic solutions containing sodium or potassium at the concentrations expected for the wine samples. Assuming that the response time is the time taken for the potential to reach a value of 1 mV from the final equilibrium potential after an instantaneous change in the analyte concentration, it was found that, in aqueous solutions, the response time of the sodium electrode was 55 s and 80 s for the potassium electrode. Although in 1% ethanolic solutions the response time was observed to be longer for both electrodes, for practical purposes, 2-min waiting-times for stable readings with both electrodes were taken as a criterion in the analysis of wine samples.

In order to obtain an adequate pH working range, series of solutions containing known concentrations of sodium and potassium were prepared with different pH values, and their potentials were measured by means of a combined glass/calomel electrode. From the results obtained and for the levels of sodium and potassium expected in wine samples, it is possible to ascertain that the optimum pH range for potassium analysis is 2·5–10·5, whereas for sodium a pH value higher than 9·5 is recommended. In the last case, the selection of a more adequate reagent for pH adjustment was studied, taking into account its possible interference with the sodium electrode. The following solutions were tested: (a) ammonium hydroxide/ ammonium chloride buffer solution, (b) 10% v/v tetrabutylammonium hydroxide solution, (c) 20% v/v triethanolamine solution. The best results were obtained with the last one in accordance with the data reported by Averill (1983).

As is well known, in ion-selective electrodes (ISE) methodology, ISA solutions are added to the samples so that the background ionic strength will be high and constant in relation to variable concentrations of the ion being sensed. For the potassium electrode, a 5M sodium chloride solution is recommended as ISA, whereas, for the sodium electrode, the same 20% v/v triethanolamine used for pH adjustment offers the best results. Both electrodes are selective but not specific since they may respond to other ions present in the wine samples. Apart from the H^+ interference, easily avoided as has been previously shown, the bibliographic data of selectivity coefficients for both electrodes (Orion Research Inc, 1979; 1981) and the contents of potassium and sodium expected in wine samples, allow prediction of the absence of mutual interference during measurements. Interference of ions such as Ag^+, Rb^+, Cs^+, is not a problem due to their low occurrence in wine samples. On the other hand, the interfering action of NH_4^+ can be disregarded if both the selectivity coefficient and the expected concentration levels of this ion in wine samples are considered.

Recommended analytical procedures

Pipet accurately 5 ml of the wine sample into a beaker, add 50 ml of deionized water for potassium determinations or 50 ml of 20% v/v triethanolamine solution for sodium determinations. The supplementary addition of 0·5 ml of 5M sodium chloride as ISA solution is necessary only for potassium analysis. Ion-selective and double junction reference electrodes, in each case with the appropriate filling solution in the outer chamber, are immersed in the stirring sample solutions, and the plastic bottle of the dispensing system is filled with the corresponding working standard solution.

Data, such as volume of sample (5 ml for both determinations), total solution volume (55 ml for sodium and 55·5 ml for potassium determinations), concentration of working standard solution (10^{-2}M for sodium and 4×10^{-2}M for potassium determinations), stability criterion (3 mV/min for both determinations), level of precision (2% for both determinations), mV increment between additions of standard solution (18 mV for both determinations), are introduced in the programmed instructions for the Multiple Known Addition method and the equipment, fully automatically produces the content of sodium or potassium in the wine sample.

RESULTS

The precision of the analytical procedures recommended was determined by their application to eleven samples of the same wine. The results obtained showed an average potassium content of 1001 mg dm^{-3} with a relative standard deviation, SD = 0·78 and 34·6 mg dm^{-3} with SD = 1·67% for sodium determination. The accuracy of the analytical procedures was tested in different wine samples with sodium and potassium contents previously determined by standard analytical methods. After several additions of known concentrations of each ion, the samples were analyzed following the recommended procedures. The percentages of recovery ranged from 99·7% to 103·7% for sodium determination and from 98·1% to 99·0% for potassium determination.

Sixty-three samples of red, rosé and white wines were taken from different wine growing areas in Spain (Jeréz, Málaga, Moriles-Montilla, Riveiro, Perelada, Penedés, Priorato, Tarragona, Alicante, Jumilla, Badajoz, Arganda, Cigales, Rueda, Valdepeñas, La Mancha, Cariñena and Rioja). The samples were cooled at 8°C in propylene containers. After applying the recommended analytical procedures, the results showed that sodium concentration ranges from 3·8 to 172·5 mg dm^{-3} with an average value of

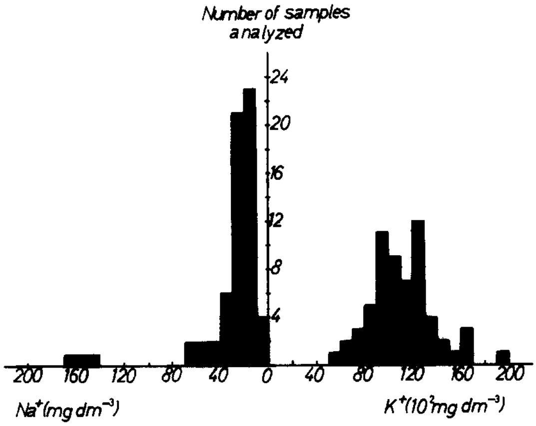

Fig. 1. Distribution of the sodium and potassium concentrations of sixty-three Spanish wine samples.

30·4 mg dm^{-3}. Although three samples showed abnormally high values, it is possible to state that there is no dispersion of the results obtained since 76% of wine samples are included in a concentration range of 10·0–30·0 mg dm^{-3}. Potassium concentration in the analyzed samples ranges from 565·1 to 1950 mg dm^{-3} with an average value of 1118 mg dm^{-3}, and a larger distribution of concentrations than in the sodium determinations. A histogram of the data obtained is shown in Fig. 1.

The wine samples were also analyzed by flame emission photometry as a reference analytical technique (AOAC, 1984) and the results compared with

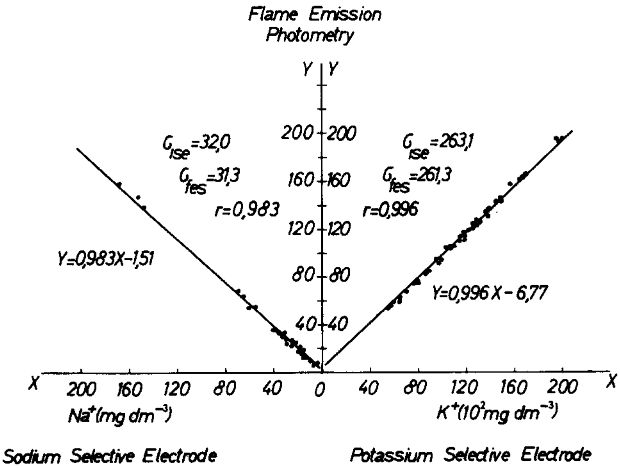

Fig. 2. Regression analysis comparing the results obtained by application of proposed and reference analytical methods on wine samples.

the data obtained by application of the ion-selective analytical procedures. Statistical treatment of the data was made with a Sinclair ZX-81 microcomputer. The equations of the fits and their deviations and correlation coefficients for sodium and potassium determinations by both instrumental techniques of analysis, are shown in Fig. 2. From the values obtained, it is possible to affirm that there is a very slight tendency to get higher values with the ISE method than with the FES method. In spite of that, a very great concordance in the experimental results was found.

CONCLUSIONS

The use of Ion-Selective Electrodes in wine analysis is a highly attractive possibility because the recommended analytical procedures require relatively inexpensive equipment, simple to operate, with a minimum of analysis time and sample size. The results obtained have shown that the procedures are precise, reproducible and capable of accurate determinations of background levels of sodium and potassium in wines. ISE methods may be a practical alternative to other analytical techniques adopted as reference methods to measure sodium and potassium in wine, as the regression analysis has proved in this study, particularly for control laboratories in the wine industry.

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