Determination of Metallic Cations in Wines by Flow Injection Analysis

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Four flow-injection manifolds were developed aiming to automate the determination of metallic cations (Na, K, Ca, Mg, Fe, Mn, Zn, and Cu) in wines using atomic absorption (AAS) and flame emission (FES) spectrometry as detection processes. Good agreement was obtained between the results of FIA methods and by the reference methods, in which samples are prepared in a discrete manner and then introduced into the detection system. The FIA methods developed present good quality results (relative standard deviation between 0.57% and 1.4%) with high sampling rates (180 to 360 samples per hour) and a low reagent consumption.

KEY WORDS: flow injection analysis, metallic cations, wines

The main importance of metallic cation determination in wine is their content influence on wine stability (2,6).

Determination of these species has been generally accomplished by atomic absorption and flame emission spectrometry (2). The measurement procedures by these methods with modern equipment is simple and quick. However, before the measuring procedures, it is necessary to carry out the preparation of the samples in accordance with the instrumental demands to avoid chemical and physical interferences. In many cases, the cation whose determination is intended is present in a higher concentration than the maximum value in which it is possible to establish a linear relationship between the concentration and the physical property that is measured. In this article, the application of flow injection analysis (FIA) is described in the automation of all operations that precede the measurements, in order to execute continuously the dilution of the sample, the addition of reagent, and the introduction of the sample in the detection system.

Materials and Methods

Instrumentation: The determinations were executed in a Pye Unicam Model SP9 atomic absorption spectrometer and in a Corning Model EEL flame emission spectrometer. In the manifold dispersion studies, a Bausch & Lomb Model Spectronic 21 spectrophotometer equipped with a Hellma Model 178.713 flow cell was used. A Metrohm Model E586 chart recorder was linked to this equipment.

Reagents and solutions: The solutions were prepared using deionized water (conductivity < 0.1 µS/cm) and chemicals of analytical reagent grade.

The standard solutions used in the establishment of the calibration graphs of each of the cationic species were prepared by rigorous dilution of BDH Chemicals standard solutions of 1000 mg/L, except the solution of cation potassium of 10 000 mg/L, which was obtained by rigorous weighing of potassium chloride previously dried at 110°C.

Flow injection manifolds: For determination of the cationic species, four flow injection manifolds were constructed as presented in Figure 1. For propulsion of the solutions, Gilson Model Minipuls 2 peristaltic pumps and pumping tubes of the same brand were used. The sample injection was made with a Rheodyne Type 50 injection valve.

In the connection between the components of the manifolds, 0.8 mm i.d. Omnifit Teflon tubing was used, as well as Gilson end-fittings and connectors and homemade Y-joints (used as confluence points or stream splitters), and pulse dampeners constructed of perspex (1).

The extension of physical dispersion (dilution) endured by the sample plug throughout the flow injection system, from the moment of injection to the entry into the detector was evaluated by calculating Ruzicka's dispersion coefficient (Dt) (8).

In the atomic absorption and the flame emission spectrometers, an apparent dispersion occurs that depends on the flow rate of entry into the nebulizer and on its configuration, so another dispersion coefficient (Dt) was calculated correspondent to the cause between the concentration of the species before the introduction into the flow system and the maximum concentration at the moment of detection (atomizer). This coefficient quantifies the joint effect of the FIA system and the detector in the diminishing of the analytical signal.

In the case of the system used for the determination of the sodium and potassium cations, it was possible to calculate only the value of Dt, since the high flow rates used made the use of the flow cell unfeasible in the spectrophotometric determination of the dye solutions used.
Fig. 1. Flow injection manifolds used in the determination of metallic cations in wines: A, sodium and potassium; B, calcium and magnesium; C, iron, manganese, and zinc; D, copper; Q, flow rates (mL/min); V, injection volume; L, tube length (cm); PD, pulse dampener; FES, flame emission spectrometer; AAS, atomic absorption spectrometer; P, peristaltic pump.

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Results and Discussion

For determination of the cations, four different manifolds were used. Their characteristics were essentially dictated by the extent of sample dilution necessary to be within detection levels of the instrument and by the eventual addition of reagents to eliminate chemical interferences.

In order to obtain high dilutions without diminishing the sampling rate, systems with a stream split were used. Additionally, a high flow rate was imposed on the entry of the nebulizer to diminish the nebulization efficiency. Under such conditions, the flow rate of entry in the nebulizer is controlled by the peristaltic pumps and not by the aspiration system of the detector, minimizing the influence of the physical characteristics of the matrices (viscosity) which in wines is fundamentally determined by its alcohol content.

The use of high flow rates, as well as a reduced sample volume (10 μL) promotes the speed and the cleansing efficiency of the system as well as high sampling rate.

For each cation, the upper limit concentration of linear response was calculated from calibration graphs. The value of the lower limit was calculated as corresponding to three times the standard deviation of the background noise obtained for the system.

**Determination of sodium and potassium:** The concentrations of these two cations in wines (2) are much higher than the upper linear response limit in flame emission spectrometry. This fact, allied to the physical characteristics of the matrix, calls for a high dispersion manifold in which the sample plug dilution coupled to the apparent dispersion occurring in the nebulizer ensures the execution of the determinations in the linear response range. For these requirements to be met, a manifold (Fig. 1A) was used with two confluence points (X and Z) and a stream split (Y).

The sample plug of much reduced volume is inserted in the carrier stream and endures, in the confluence point X immediately after the point of injection, a first dilution, which is greater in the potassium determination than in sodium determination (see flow rates in Fig. 1A). From this confluence point, there occurs an increase in transport velocity throughout the 200-cm tube, continuing the sample dispersion in the carrier until the stream split, Y, in which the sample plug is sectioned, and the flow rate is reduced in the interior of the manifold. The use of a stream split is advantageous, as it allows the quicker dilution of the central portion of the sample plug by action of the axial dispersion which takes place throughout the 30-cm tube and the increase of the dispersion in confluence point Z. A consequent decrease in the quantity of the sample to be determined reduces the peak enlargement provoked by the axial dispersion, which contributes to the attainment of a good sampling rate.

Confluence point Z promotes the increase of the physical dispersion and a significant rise in the value of the flow rate to nearly 27 mL/min in the determination of sodium and 25 mL/min in the determination of potassium, significantly superior to the nominal flow rate of the flame emission spectrometer aspiration system (ca 7.5 mL/min).

With this manifold, it is possible to execute determinations in the samples that contain sodium between 3mg/L and 200 mg/L and of potassium between 23 mg/L and 2000 mg/L operating in a linear response range between the value of the analytical signal and the concentration of the sample, with a sampling rate of 200 and 180 samples per hour, respectively.

**Determination of calcium and magnesium:** To execute continuously, the necessary operations of adequacy of the samples to the measuring system of a manifold (Fig. 1B) with two confluence points (X and Y) and a stream split (Z) was used.

In confluence point X, located immediately after the injection point, the sample plug inserted in the carrier...
stream endures an initial dilution, while simultaneously a flow rate increase is produced, producing a subsequent sample dispersion in the carrier throughout the 200-cm tube.

The lanthanum chloride solution (13500 mg/L concentration) used to eliminate chemical interference is added in the confluence point Y. This concentration was chosen from the dilution evaluation of this solution between confluence point Y and the entrance into the detector so that at this point its value would be approximately equal to the reference method (4). After the confluence point Y, the dispersion continues along the 30-cm tube to the stream split Z, where the sample plug is sectioned and led to the detector with a flow rate (9.0 mL/min) that is superior to the aspiration system of the atomic absorption spectrometer.

This manifold allows determinations in samples that contain calcium between 1.4 and 200 mg/L and of magnesium between 0.9 and 200 mg/L, with a sampling rate of 240 samples per hour and a lanthanum consumption of 30 samples per hour. The reproducibility of the results obtained by FIA methods was evaluated comparing them with those obtained by the reference procedures (C,) referenced in Table 1, in which the samples are prepared in a discrete manner and subsequently measured using the detection systems in a conventional manner. For all cationic species studied, determinations for 30 samples of various types of Portuguese wines (Ports, reds, and whites) were carried out. With this set of values, a relationship of the type C, = C + SC, was established (results presented in Table 1). These allow the conclusion that good agreement exists between the values obtained by FIA and those obtained by the reference methods.

Determination of iron, manganese, and zinc: In the determination of these three cations, a manifold (Fig. 1C) of low dispersion was developed, with a stream split after the insertion point of the sample and a tube with enough length to obtain the required dispersion to execute the measures in a linear response range. The physical interferences of the matrix were minimized by using a flow rate at the entrance of the atomizer (10.0 mL/min) superior to the aspiration system of the detector.

This manifold allows the determinations, operating in a linear response range, for concentrations of iron between 0.09 and 20.0 mg/L, of manganese between 0.1 and 6.0 mg/L, and of zinc between 0.03 and 2.0 mg/L, with a sampling rate of 240 samples per hour for iron and 360 samples per hour for magnesium and zinc.

It should be emphasized that in the event that samples contain higher cation levels than the ones mentioned, the upper linear response limit could be increased simply by lengthening the tube, which would, however, reduce sampling rate.

Determination of copper: Since the copper content in wines (2) is usually within the concentration limits in which the atomic absorption measures are currently made for this cation (many times even near the detection limit), a manifold was designed (Fig. 1D) with only one channel to simply proportion the transport and the introduction of the sample into the detector, minimizing dispersion. Since the dilution endured by the sample is much reduced (D = 1.5), using a flow rate superior to the aspiration system of the atomic absorption spectrometer was imperative for the value of the signal obtained not to be influenced by the physical characteristics of the matrices. However, this flow rate only exceeded ca 0.5 mL/min that of the nominal flow rate of the detector, so that a significant decrease of the analytical signal was not obtained and consequently the detection limit would not deteriorate, which in the case of this determination is critical. The value of this obtained limit for the system was 0.04 mg/L, which is satisfactory since it is less than the copper content of the wines (2) of most countries. The maximum linear response limit is 4 mg/L with a sampling rate of 360 samples per hour.

Comparison with the reference methods: The quality of the results obtained by FIA (C,) methods was evaluated comparing them with those obtained by the reference procedures (C,) referenced in Table 1, in which the samples are prepared in a discrete manner and subsequently measured using the detection systems in a conventional manner. For all cationic species studied, determinations for 30 samples of various types of Portuguese wines (Ports, reds, and whites) were carried out. With this set of values, a relationship of the type C, = C + SC, was established (results presented in Table 1). These allow the conclusion that good agreement exists between the values obtained by FIA and those obtained by the reference methods.

The reproducibility of the results was evaluated by calculating the relative standard deviation from the 10 determinations repeated on a sample whose concentration in the cation in question is indicated in Table 1. It was verified that the reproducibility of the FIA method is slightly higher than that of the reference procedures.

Conclusions

The FIA methods developed for metallic cation determination in wine constitute a good alternative to the current processes in which the sample is prepared in a discrete manner, since they provide good quality results with high sampling rates.

The use of the FIA system developed for the determination of calcium and magnesium permits an appreciable saving of reagent to eliminate chemical interferences (lanthanum consumption ca four times less than the reference method).

The imposition of a flow rate in the entry of the nebulizer superior to that of the aspiration systems of the flame emission and the atomic absorption spectrometers provides an expeditious and efficient way to minimize the physical interferences of the matrices and a simple way to diminish the analytical signal. When only the first objective is intended, a slightly greater flow rate than that of the aspiration system of the detector should be used to avoid an undesirable and significant decrease of the analytical signal.

The modular composition of the FIA systems grants them versatility, allowing quick set-up and/or dismantling of a system (ca 2 min); the time between connection of the peristaltic pumps and the first determination is not more than one minute.

The implementation of these FIA systems in laboratories where these determinations are currently executed using the aforementioned detection systems is accessible, since the materials used are simple, inexpen-

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sive, and easily maintained and do not require specialized technicians.

**Literature Cited**


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