



ELSEVIER

Journal of Chromatography A, 881 (2000) 645–650

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination of lithium in wines by ion chromatography

O. Zerbinati^{a,*}, F. Balduzzi^a, V. Dell'Oro^b

^a*Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale "A. Avogadro", Corso T. Borsalino 54, I-15100 Alessandria, Italy*

^b*Istituto Sperimentale per l'Enologia di Asti, Laboratorio Revisione Analisi, Via P. Micca 35, I-14100 Asti, Italy*

Abstract

Lithium ion can be added as a denaturing agent to wines unsuitable for consumption. Accuracy of flame atomic emission spectroscopy with direct nebulization, which is commonly adopted for discovering illegal use of denatured wines, was found to be compromised by Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} and ethanol contained in wine. Ion chromatography (IC) was tested in order to propose an alternative method for legal controls. Experimental design was used to investigate the influence on the accuracy of the determination of Li^+ at ppb levels, of Na^+ and ethanol content of wine and of fluctuations of eluent flow-rate and composition. It turned out that IC quantification of Li^+ can be affected by eluent parameters rather than by wine composition. Since the former can be maintained under the operators control, while the latter cannot, IC was judged preferable to AES for legal controls of Li^+ in wines. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Wine; Food analysis; Lithium; Metal cations

1. Introduction

Lithium ion is present in wines due to plant roots uptake or to storage in glass bottles. The concentration of this element normally ranges from 5 to 50 $\mu\text{g l}^{-1}$ [1–8]. Considering its very low natural concentration, lithium is used in Italy as denaturing agent, to mark wines not allowed for consumption. The control of frauds is normally effected by flame atomic emission spectroscopy (AES) with direct nebulisation, which is the official method of analysis prescribed by Italian law. Although Italian wines are exported in large quantities, no official method of analysis for lithium in wines has been adopted as yet by international organisations.

Inorganic mono- and divalent cations, other than

Li^+ , are normally present in wines at concentrations ranging from 10 to 1500 ppm, depending on the element and on wine's origin. These cations are likely to affect the accuracy of AES determination of lithium ion, and further inaccuracy can derive from ethanol content of wines. Therefore an alternative method of analysis, not affected by the composition of wine matrix, would be of help in legal procedures for combating fraud.

Ion chromatography (IC) with conductivity detection, which is commonly used for determining alkaline and alkaline-earth cations in solution, may be less subject than AES to interference from other cations contained in wine, since the Li^+ peak can be isolated quite well. Nevertheless, IC quantitative data could be influenced by chromatographic conditions, such as eluent flow-rate and composition, therefore an investigation on IC performance seems worth being conducted. In this work, Li^+ determination by

*Corresponding author.

E-mail address: zerbinati@ch.unito.it (O. Zerbinati)

AES and IC were compared and the factors which limit the accuracy of both were investigated.

2. Experimental

2.1. Materials

High-purity lithium, sodium, potassium, magnesium, calcium and ammonium chlorides, nitric and methanesulfonic acid (MSA) were purchased from Sigma–Aldrich (Milan, Italy). 500 mg, C₁₈ silica solid-phase extraction (SPE) cartridges were obtained from Merck (Bracco, Milan, Italy). Utrapure water produced by an Elga-Stat (Elga, High Wycombe, UK) purification apparatus was used for preparing standard solutions and chromatographic eluents. Ion chromatographic measurements were performed by a Dionex DX500 (Dionex, Sunnyvale, CA, USA) IC system equipped with an ED40 conductometric detector, an electrochemical suppressor, a CS12 250×4.6 mm analytical column and a CG12 guard column. Aqueous methanesulfonic acid, at concentrations ranging from 18 to 22 mM and at flow-rates ranging from 0.9 to 1.1 ml min⁻¹ was used as eluent. AES measurements were effected by means of a Varian Spectr AA 10 plus (Varian Australia, Mulgrave, Australia) spectrophotometer, which was operated at 670.8 nm in atomic emission mode with an acetylene–air flame.

2.2. Sample pre-treatment

Samples were acidified with 0.1% nitric acid before AES measurements. For IC, preliminary analyses were performed on some wine samples, in order to explore practical applicability of this technique. It was observed that direct injection of samples, without any pre-treatment, required a long time for after run baseline stabilisation. For this reason, a preliminary clean-up procedure was adopted in order to retain those components, probably organic, responsible for long after run stabilisation times. Wine samples (2 ml) were passed through C₁₈, 500 mg SPE cartridges before analysis. No conditioning of SPE cartridges was effected, to avoid unwanted dilution of the samples caused by conditioning solvent residues. Variation in the area of the

Li⁺ peak of standard solution, after passing them through the SPE cartridge, lay within 2%, which was the same standard deviation (SD) observed for replicate IC analyses. Fig. 1 shows the chromatogram of a wine sample, where it can be observed that Li⁺ is well resolved from the remaining cations and that the baseline becomes stable within a reasonable time after analysis.

3. Results and discussion

3.1. Atomic emission analyses

Table 1 reports the results of the determination of lithium concentration of standard solutions by direct nebulisation AES. Column A shows the results obtained with 1000 ppm aqueous solutions of some of the major mono- and divalent cations of wines, where Li⁺ ion was not added. It can be seen that all cations simulate to some extent the signal of the Li⁺ ion, although no peak was found for this element when the same solutions were analysed by IC. In particular, 1000 ppm calcium ion produced a signal equivalent to that of 51 ppb lithium. The apparent concentrations measured on 25 ppb standard lithium solutions added to 1000 ppm cations are reported in column B. It can be seen that all cations produced positive errors in the determination of lithium, and therefore their effects are additive. Due to the high levels of potassium in wines and to the intense effect of calcium, these last two cations are likely to produce the most significant effects on the AES accuracy. Quantification by means of standard addition method could compensate inaccuracies due to matrix effects, which contribute to the errors of column B, but cannot correct the interferences reported in column A.

Fig. 2 shows the effects of increasing concentration of Ca²⁺ ion on the percent error in the determination of 25 ppb Li⁺. It can be seen that this error is significant at concentrations ranging from 50 to 200 ppm, which are usual in wines, whichever of the available slit widths was used.

The effect of some of the major organic components of wine matrix were also investigated. 10–200 ppb Li⁺ standard solutions in a synthetic wine matrix, containing 12% (v/v) ethanol, 7.5% and 0.5

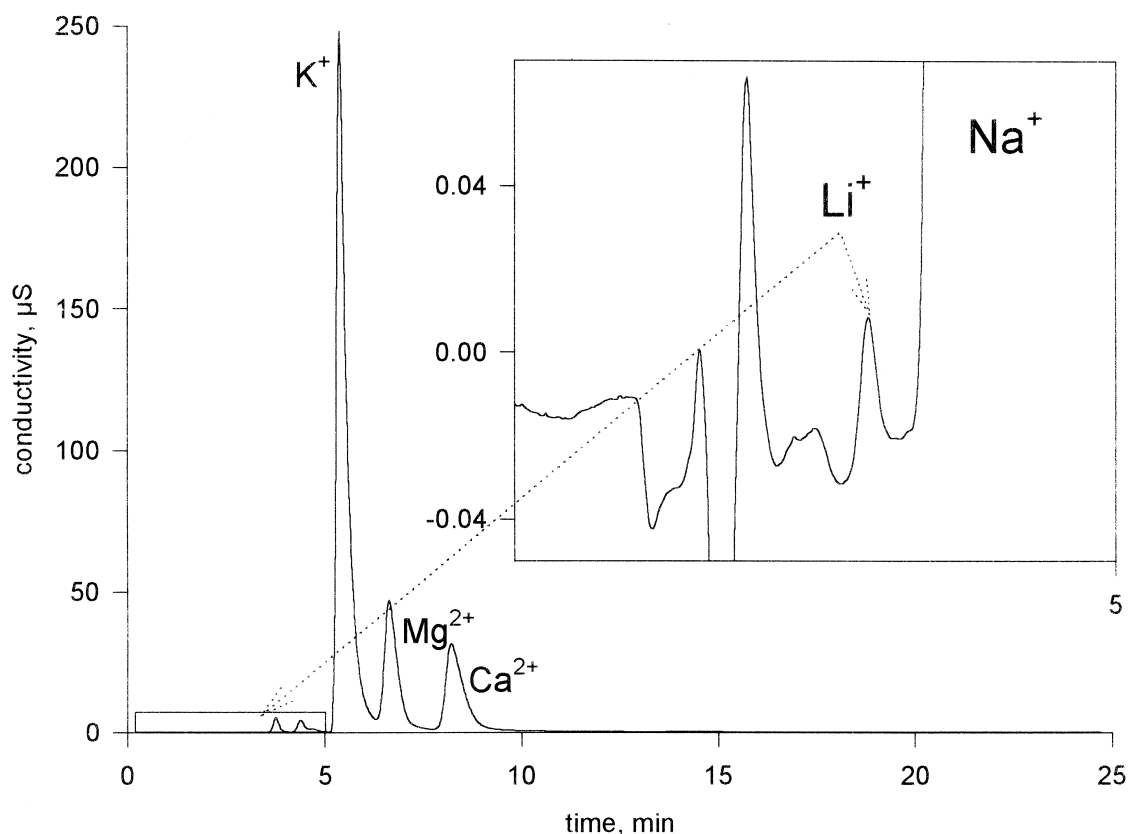


Fig. 1. Ion chromatogram of a red wine sample after SPE clean-up. CS12 250×4.6 mm analytical column and CG12 guard column. Eluent: 20 mM methanesulfonic acid, flow-rate: 1 ml min⁻¹, 25 µl injection volume.

(w/w) glucose and tartaric acid, respectively, were analysed by AES. The average intensity of emission signals obtained was 90% (S.D. 4%, $n=6$) with respect to that of solutions prepared in ultrapure

water. Although the effect of organic components is negative in sign, it is unlikely that it can exactly compensate positive interference of cations, due to the large variability of wine composition.

Table 1

Column A: apparent Li⁺ concentrations (ppb) given by 1000 ppm solutions of the indicated ion; column B: results of AES determination of 25 ppb Li⁺ added with 1000 ppm of each ion; column C: percent error on the determination of 25 ppb Li⁺; column D: ranges of normal concentrations in wines, ppm^a

Interfering ion	A	B	C	D
Mg ²⁺	3 (1)	30.0 (0.1)	+20.0	20–200
Ca ²⁺	51 (3)	75.3 (0.1)	+201	50–150
Na ⁺	4.8 (0.3)	35.6 (0.2)	+42.4	10–150
NH ₄ ⁺	2 (1)	35 (1)	+40	10–100
K ⁺	3.8 (0.3)	37 (1)	+48	500–1500

^a Instrumental conditions: wavelength: 670.8 nm; slit aperture: 0.5 nm. Standard deviations indicated in parentheses ($n=6$).

3.2. Ion chromatographic analyses

Four experimental factors, which might interfere with IC lithium determination, were chosen for investigation. Among the wine composition factors, sodium and ethanol concentrations were considered worth investigating, the former due to the nearness between the peaks of lithium and sodium, the latter because it might alter the shape of lithium peak, which elutes close to void time. Among the instrumental factors, eluent composition and flow-rate were chosen for investigation, since it was presumed that they may influence performances of IC quantita-

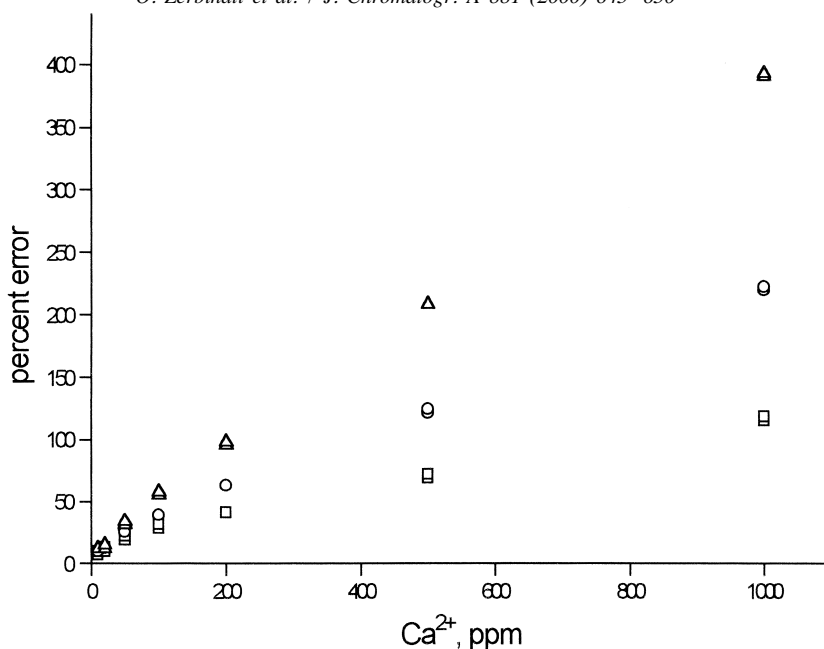


Fig. 2. Effect of calcium concentration on the percent error of 25 ppb Li^+ determination by AES, by using three different slit apertures. □: 0.2 nm; ○: 0.5 nm; △: 1 nm.

tion. Lithium peak height and area were chosen as the experimental responses.

Instead of univariate experiments, in which the effect of each factor is studied individually, multivariate experiments were programmed by means of two-level experimental design, in order to minimize the number of experiments and to collect information about interactive effect of factors. A 2^4 full factorial design was used to test effects on experimental responses of the concentrations of Na^+ , ethanol and methanesulfonic acid concentrations. 50 ppb Li^+ standard solutions were prepared according to the scheme reported in Table 2 and were injected in triplicate. The main effects on both peak heights and area were calculated from the experimental responses and are reported in Table 3. It can be seen that the variables related to wine composition exert a limited effect on both peak height and area, while instrumental conditions affect strongly both these experimental responses, and particularly peak area. This means that the accuracy of the analysis is influenced less by wine composition variables than by instrumental parameters. It is quite easy to control eluent com-

position and flow, while it is impossible to control wine composition. Considering that the 20% span of flow-rate and methanesulfonic acid concentrations are larger than occasional fluctuation which can occur under appropriate operative control, the advantage of IC with respect to AES is evident. Binary interactions were also calculated, and their values ranged from 0.7%, for interaction of ethanol concentration and flow-rate on peak height, to 8.7% for interaction of Na^+ and ethanol concentration on peak area. Considering the data reported in Table 3, it is quite evident that area response is more sensitive than height to the variation of the experimental factors.

A 2% standard deviation of the IC height and area was obtained by injecting standard Li^+ solutions of concentrations ranging from 10 to 200 ppb ($n=6$), while 0.7% standard deviation was obtained by AES measurements on the same solutions. Average standard deviations of IC data obtained from experimental design measurements were 4% and 3%, respectively, while no comparable standard deviation was measured for AES. Although AES is more precise

Table 2
Scheme of 2⁴ experimental design^a

Experiment	[Na ⁺] (ppm)	[Ethanol] (%)	[MSA] (mM)	Flow (ml min ⁻¹)
1	–	–	–	–
2	+	–	–	–
3	–	+	–	–
4	+	+	–	–
5	–	–	+	–
6	+	–	+	–
7	–	+	+	–
8	+	+	+	–
9	–	–	–	+
10	+	–	–	+
11	–	+	–	+
12	+	+	–	+
13	–	–	+	+
14	+	–	+	+
15	–	+	+	+
16	+	+	+	+

^a [Na⁺]: 10 ppm = “–”; 150 ppm = “+”; [ethanol]: 10% = “–”; 20% = “+”; [MSA]: 18 mM = “–”; 22 mM = “+”; flow-rate: 0.9 ml min⁻¹ = “–”; 1.1 ml min⁻¹ = “+”.

than IC for the analysis of standard solution, IC seemed the most robust when real samples were analysed.

4. Conclusions

Direct nebulisation flame AES and IC were compared in order to ascertain which is the best technique for determining the concentration of lithium in wines for legal controls. AES accuracy proved to depend on wine composition, since it showed severe positive interference from inorganic cations, especially calcium and potassium, and negative interfer-

ence from glucose and ethanol, two major organic components of wine. Although these interferences are opposite in sign, there is little probability that they can compensate each other due to the large variability of wine composition. Further, these errors cannot be entirely corrected by means of standard addition method. The effects of sodium and ethanol concentration in wine and of flow-rate and eluent composition on the accuracy of IC determination, were also tested by means of multivariate experimental design. It emerged that the accuracy of IC determination is less sensitive to wine composition than to instrumental conditions, which can be effectively controlled. Solid-phase clean-up of samples was used for accelerating after run baseline stabilisation, since it did not affect lithium determination. Therefore IC seemed preferable to AES for legal controls of lithium concentration in wines.

Table 3
Main effects of the four factors on height and area of Li⁺ peaks, percent units

	Factor	Height	Area
1	[Na ⁺]	5.3	5.3
2	[Ethanol]	2.1	8.0
3	Flow-rate	1.2	32.9
4	[MSA]	96.8	112.3

References

- [1] B. Medina, P. Sudraud, *Ann. Fals. Exp. Chim.* 72 (1979) 65.
- [2] M. Munoz, A. Iunca, J. Guasch, M.S. Larrechi, F.X. Rius, G. Scarponi, *Ric. Vitic. Enol., Conegliano* 5 (1987) 208.

- [3] K. Hariju, P. Ronkainen, Z. Lebensm. Unters. Forsch. 170 (1980) 445.
- [4] M.J. Latorre, C. Garcia-Jares, B. Medina, C. Herrero, J. Agric. Food Chem. 42 (1984) 1451.
- [5] M. Ney, Ann. Fals. Exp. Chim. 58 (1965) 263.
- [6] C. Baluja-Santos, A. Gonzalez-Portal, J.M. Bouzas-Bouzas, Anal. Chim. Acta 196 (1987) 283.
- [7] A. Volgaropoulos, T. Soulis, *Connaiss. Vigne Vin* 21 (1987) 23.
- [8] F.S. Interesse, G. D'Avella, G. Alloggio, F. Lamparelli, Z. Lebensm. Unters. Forsch. 181 (1985) 470.