

Quantification of CO₂ in wines with piezoelectric crystals coated with tetramethylammonium fluoride and comparison with other methods

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Abstract. A quartz crystal coated with tetramethylammonium fluoride tetrahydrate is used for the quantification of carbon dioxide. The performance of the method was compared with another method using crystals coated with N, N, N', N'-tetrakis (2-hydroxyethyl) ethylenediamine, and with a titrimetric method. The proposed method is faster and more precise than the titrimetric method, and much faster (around 15 times) than the other method using piezoelectric crystals.

Key words. Quartz crystal microbalance, piezoelectric crystals, wine, carbon dioxide.

Introduction

A quartz crystal microbalance (QCM) has been already used for the quantification of CO₂ in wine [1]. The previously reported method was more precise than the titrimetric, although it suffered from a serious drawback: the short duration of the validity of the calibration. In fact, the frequency of a crystal coated with N, N, N', N'-tetrakis (2-hydroxyethyl) ethylenediamine (THEED) changes along time, and so does the crystal sensitivity.

It is known that tetramethylammonium fluoride tetrahydrate (TMAF) can be used as a very stable crystal coating for CO₂ determination [2], and, in spite of its slightly lower sensitivity to CO₂ than THEED, it can be used for the quantification of CO₂, at least for a three weeks period, without being recalibrated, which leads to an improvement of the previous QCM method.

Experimental

Apparatus

Crystals were coated on both sides with a solution of TMAF in absolute ethanol with an airbrush (Badger Model 200) [3].

Although the general layout of the method based on crystals coated with THEED [1], was maintained, significant changes had to be made, both in the wine cell, and in the sample introduction procedure.

As can be seen in figure 1, in the new method, the wine cell is a glass reservoir with a glass sintered plate at the bottom, to sustain the wine, and to allow a flow of nitrogen. As this cell is much smaller (it was constructed for volumes of 0.5 cm³ of wine) than the one used in the previous methodology, a bulb with a glass spike was designed to prevent liquid bubbles from reaching the top of the cell.

The wine samples were introduced with a syringe through a silicone septum G14, located at the top of the cell, while pure CO₂, for standards, was injected through an Omnifit (Ref. 3301) septum injector, located before the wine cell.

The piezoelectric crystals were 9 MHz (SIWARD) and the frequency was monitored with a Universal Counter Board (Keithley MetraByte Corporation), and the data were stored in an ASCII file format.

Reagents

TMAF (Aldrich 10,721-2) was dissolved in ethanol (Merck 11727). The compounds tested for interferences (acetic acid,

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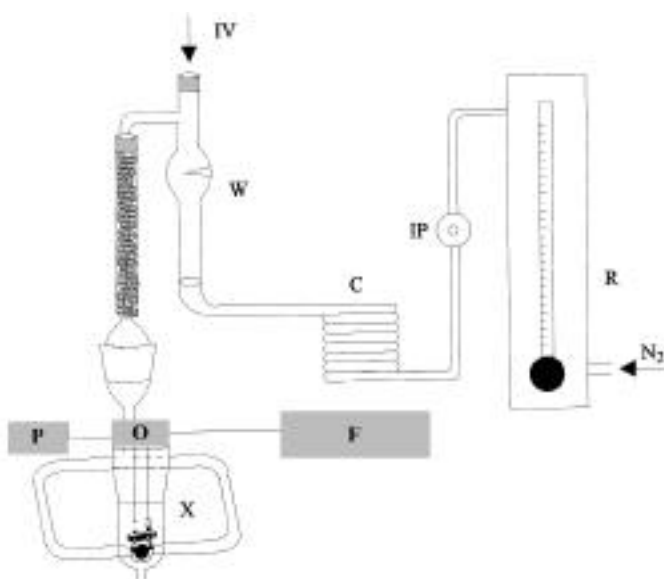


Fig. 1. Experimental layout (X: crystal cell; P: power supply; O: oscillator; F: frequency meter; W: wine cell; IV: sample introduction; C: coil; IP: injection port; R: flowmeter).

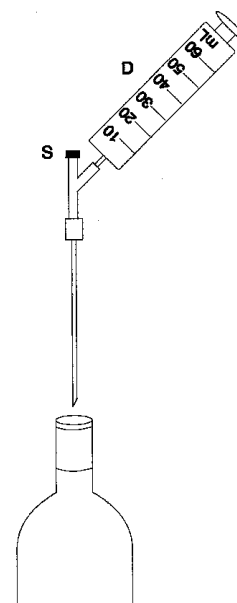


Fig. 2. Sampling apparatus used for wine with CO_2 content above $1000 \mu\text{g cm}^{-3}$ (S: sampling septum; D: drawing syringe).

ethyl acetate, ethanal, ethanol, methanol, 3-methyl-1-butanol and 2-methyl-1-propanol) were all p.a. grade. SO_2 was generated by the addition of hydrochloric acid (Riedel-de-Häen 30721) over sodium sulphite (Merck 6652) and dried over silica-gel.

Nitrogen was R grade and carbon dioxide was N45, both from “ArLíquido”.

The wines were all still white wines produced in Portugal.

Procedure

The piezoelectric crystals were coated, on both faces, with 1% (w/v) solutions of TMAF in absolute ethanol, with a spray described elsewhere [3]. A permanent and constant flow of $30 \text{ cm}^3 \text{ min}^{-1}$ of nitrogen was maintained through the crystal cell.

Standardisation was accomplished by injecting known CO_2 volumes into the nitrogen flowing through 0.50 cm^3 of decarbonated wine. The observed frequency decrease was proportional to the CO_2 injected. The samples of wine were injected on the top of the empty wine cell. The volume of wine introduced was such that a frequency decrease near the centroid of the calibration line was observed.

For wines with CO_2 content lower than $1000 \mu\text{g cm}^{-3}$, the samples were collected from a small Erlenmeyer that was previously filled up from a chilled bottle, and closed with a rubber septum. After the wine sample reached room temperature, samples with volumes ranging from 0.050 cm^3 to 0.500 cm^3 , were collected with a syringe through the septum. For wines with higher CO_2 content, greater care was taken to avoid CO_2 losses. The sampling was accomplished with a home-made device, shown in figure 2. The bottle cork was perforated with a thin steel tube connected to a glass tube “Y” shaped, 4 cm long, with a syringe at one arm, and

a septum on the other. After filling the whole device with wine, the sample contained in the Y-tube could be withdrawn, with a syringe, through the septum.

In the titrimetric method, the Goranov procedure [4] was closely followed, for wines with CO_2 content lower than $1000 \mu\text{g cm}^{-3}$. After opening the chilled wine bottle, an aliquot of wine was transferred, with a cooled pipette, to a beaker containing a known amount of sodium hydroxide, always with the pipette tip submerged, to avoid losses of the gas. Another wine sample was degassed through boiling, and sodium hydroxide was added. Both samples were then titrated with standardised sulphuric acid, between pH 8.6 and 4.0.

For samples with higher CO_2 content, and also in the titrimetric method, the sodium hydroxide was directly added to the wine bottle [5,6]. Besides, carbonic anhydrase was added to the wine samples in order to prevent CO_2 from escaping, as it catalyses CO_2 hydration [7].

Results and discussion

Figure 3 shows the frequency of a crystal, coated with TMAF, before, and after, the introduction of a wine sample. The unusual shape of the signal, which includes a quick raise in the frequency, can be explained by the liquefaction of the CO_2 absorption product, as explained elsewhere [2].

In previously reported experiments with THEED [1], the sample introduction gave rise to an increase in the frequency, which interfered in the analytical signal. As, in this new method, the volumes of the introduced wine samples were markedly reduced, no pressure signal was observed. The elimination of this interference obviates the need to perform blank experiments, and decreases the analysis time.

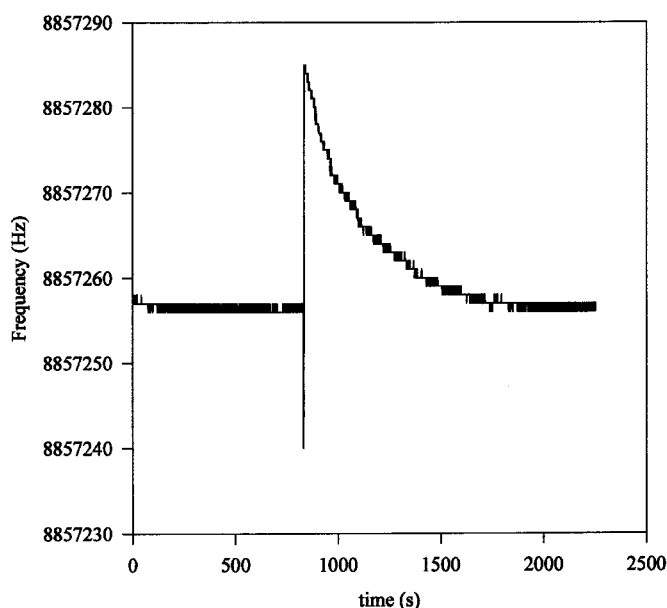


Fig. 3. Frequency of a crystal coated with TMAF, before and after the introduction of 0.300 cm³ of wine.

Table I. Results for CO₂, obtained by the analysis of 16 different wines, by QCM-TMAF and titrimetric methods (5 replicates for each wine).

Wine Sample	Titrimetric method		QCM-TMAF method	
	Median (μg cm ⁻³)	Range (μg cm ⁻³)	Median (μg cm ⁻³)	Range (μg cm ⁻³)
A	213	21	220	3
B	218	39	217	3
C	585	107	533	7
D	260	64	262	3
E	73	38	74	1
F	205	51	219	4
G	837	77	801	13
H	1003	77	962	19
I	738	34	740	13
J	201	21	209	3
K	956	43	981	19
L	1276	38	1295	18
M	1942	34	1951	20
N	1763	26	1689	18
O	794	72	851	12
P	939	111	952	14

For this low sample volumes, as experiments confirmed, the SO₂ does not interfere. This brings a concomitant advantage: the avoidance of adding H₂O₂ to oxidise the SO₂.

To test for interferences, the most important volatile constituents of wine were mixed with deaerated wine, in concentrations slightly higher than the legal limits or the ones usually found in wine, and introduced in the cell. No fre-

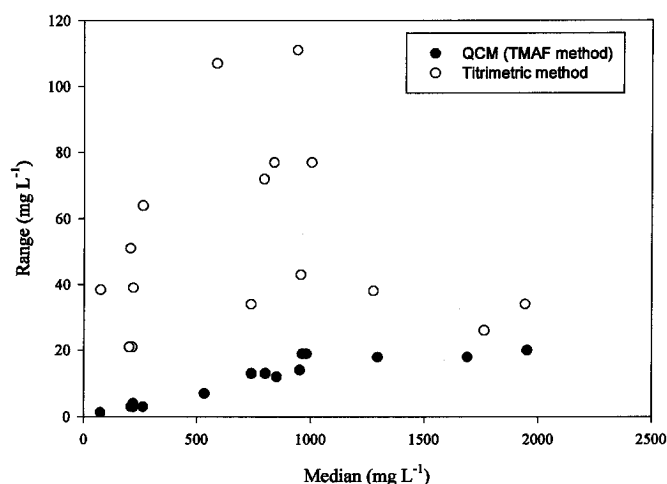


Fig. 4. Range of the results obtained for each method versus the obtained quantity of CO₂.

quency change was observed with any of the following compounds: acetic acid, ethyl acetate, ethanal, ethanol, methanol, 3-methyl-1-butanol and 2-methyl-1-propanol.

Table I shows the results obtained from the analysis of 16 different wines, performed both by the QCM-TMAF and titrimetric methods. Figure 4 shows the range of the results (difference between maximum and minimum value obtained with 5 replicate analysis of the same wine), obtained for each method versus CO₂ content. While for the QCM-TMAF method, and for a CO₂ content smaller than 1000 μg cm⁻³, the precision of the analysis, expressed by the range of the results, shows a small increase with the CO₂ concentration, the precision for the titrimetric method shows a greater variability and no trend can be found. A better precision can be assigned to the QCM-TMAF method, as the range of the results is always smaller. For CO₂ content above 1000 μg cm⁻³, the range of the results obtained by the titrimetric method became close to the QCM method, although always higher.

As a general conclusion it can be said that the new method is more precise than the titrimetric method for the analysis of still white wines. For wines with low CO₂ content, the usual methods available for the CO₂ analysis show a poor performance [7], in concentration range where QCM method already proved to work well [1]. The results now presented highlight that the QCM-TMAF method can also be applied for concentrations above 1 000 μg cm⁻³.

Furthermore, the modification of the previous QCM-THEED method [1] shows marked advantages. As a major achievement, it should be pointed out the reduction of the time of analysis from 15 hours (6 standards and 5 replicates), to 1 hour for each wine (5 replicates), not taking into account the calibration procedure. A single calibration line was used for all the 16 wines analysed with the QCM-TMAF method.

The method now proposed is thus, not only more precise than the titrimetric, but faster.

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