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Short communication

Determination of tartaric acid in solid wine residues by capillary electrophoresis and indirect UV detection

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Abstract

Tartaric acid, used in pharmaceuticals and industrial food preparation, is an important by-product of wine preparation. It is produced by wine factories in large quantities and cannot be rejected into the environment. Wineries precipitate tartaric acid using calcium hydroxide and then evaporate the mixture. The raw compact powder obtained, which contains calcium tartarate and a lot of other constituents (sugars, tannins, etc.) is sold to factories which purify tartaric acid. The different analytical methodologies which are used to determine the tartaric acid concentration in the solid wine residues are long and tedious (Goldenberg method, 14 samples per day). They also suffer from poor reproducibility. Some other methods use ion chromatography or solid Fourier transform IR, which are not currently used for such topics. We propose a capillary electrophoresis method, which not only is very quick (2 min of analysis) but also highly reproducible. Finally it provides very simple electropherograms. The intra-day and inter-day repeatability, the inter-person reproducibility and recovery were estimated. They demonstrate the ruggedness of this new method.

Keywords: Tartaric acid; Organic acids; Indirect UV detection

1. Introduction

The R–R(+)-tartaric acid, which is exclusively a natural product, is extracted from lees of wine. A large volume of this acid ($3 \cdot 10^7$ kg/year worldwide) are used in food and pharmaceutical industries [1]. Moreover it is produced by wine factories in large quantities and cannot be rejected in the environment. Therefore, wineries precipitate tartaric acid as a by-product of wine, using calcium hydroxide on wine residues and then evaporate the mixture [2]. The compact raw-powder (Fig. 1) which is obtained, contains calcium tartarate and a lot of other soluble and insoluble constituents (sugars, tannins, etc.). It is sold to factories which purify tartaric acid. One of the advantages of the tartaric acid market is that the price of this acid is very stable over time, These factories asked to know the grade (g/g) of tartaric acid in the raw calcium tartarate powder.

Several methods of quantification are described. The reference method, which uses dissolution of the rough powder in an HCl solution, precipitation of the acid and then quantification using sodium hydroxide, is old [3]. This method was improved by Mourges and Maugenet [4]. Almela et al. presented a method in which the absorption of the red colour solution obtained when sodium meta-vanadate reacts with tartaric acid is measured [5]. Tusseau and Benoit described a method using HPLC after filtration and purification of samples on Sep-Pak C_{18} [6]. More

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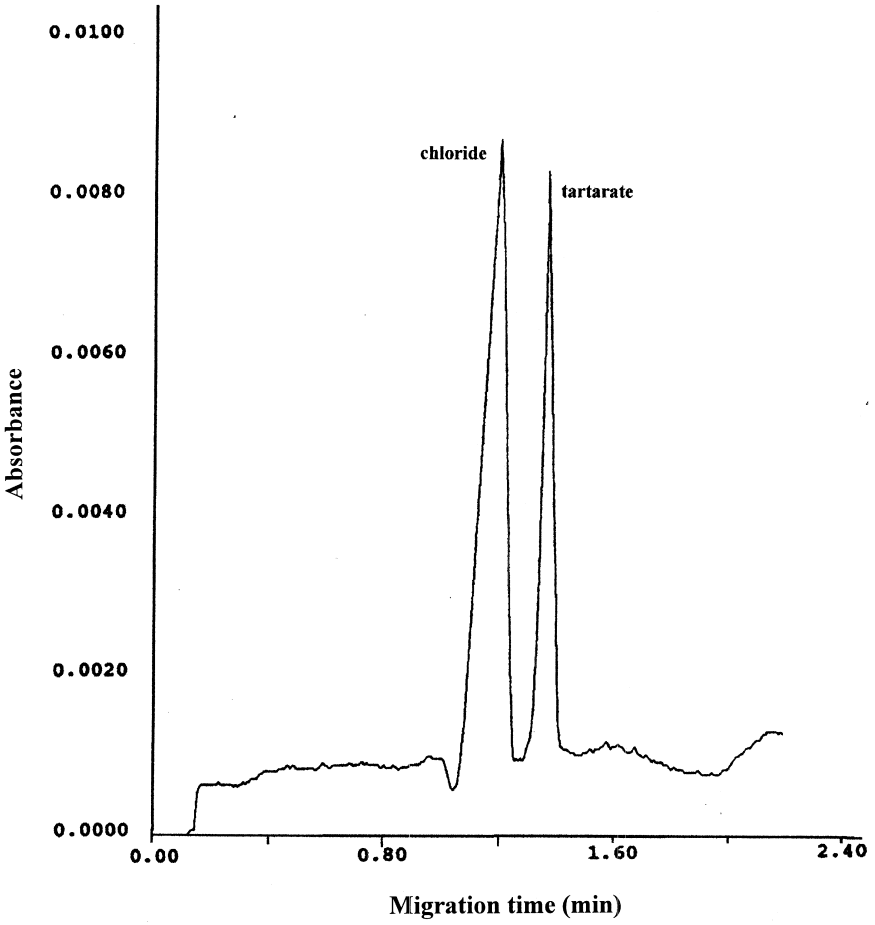

Fig. 1. Electropherogram of a calcium tartarate sample. Conditions are indicated in the text.

recently Bouvier et al. used Fourier transform (FT) IR of the rough powder to determine the concentration of tartaric acid directly [7]. Some months ago we developed in the laboratory a method to quantify organic and inorganic acids in wine using dilution of wine and analyzing acids with capillary electrophoresis and indirect UV detection [8,9]. This method uses pyromellitic acid as chromophore. In this work we will describe a method to study tartaric acid in raw powder.

2. Materials and methods

The CE system is a Fast Impact from Europhore (now Picometrics, Montlaur, France), equipped with a Thermo-Separation product date system. The fused-silica capillary is 37 cm length, and 30 cm length from the injection point to the detection window. Every day, the capillary was cleaned for 3 min with 0.1 *M* sodium hydroxide, 3 min with distilled water, 3 min with buffer. Between each run, it was cleaned according to the following procedure: 1 min with 0.1 *M* sodium hydroxide, 1 min with distilled water, 1 min with buffer. The buffer consists of 12 m*M* benzoic acid, 10 m*M* histidine, 1 m*M* tetradecyltrimethylammonium bromide (TTAB). The pH is adjusted at 5 using a solution of 1 *M* NaOH. The voltage is −11 kV producing a current of 15 μA. Indirect UV detection was recorded at 260 nm.

One hundred g of the raw powder of calcium tartarate (Distillerie d'Arzens, France) is pound using a mortar. 50 mg of the fine powder obtained is dissolved in 1 ml of a 3.6% HCl solution in a 100 ml

Table 1
Calibration of tartaric acid

Calibration curve	Slope	Intercept	R^2	RSD of slope, % ($n=16$)	RSD of intercept, % ($n=16$)
$A=f[C]$	83 160	−4484.3	0.9981	0.23	0.31
$A/T_m=f[C]$	59 374	−2864.0	0.9991	0.15	0.17

gauged flask filled with distilled water to 100 ml. The samples are sonicated for 15 min, then diluted five times with distilled water and analyzed in CE. The 1 g/g standard solution is prepared following the same protocol. From 50 mg of pure tartaric acid, this solution is diluted to obtain 0.8; 0.6; 0.4 and 0.2 g/g standard solutions. The sample and standard are hydro-dynamically injected during 1 s.

3. Results and discussion

When the raw-powder was dissolved in the HCl solution, we obtained a slurry, slightly opaque and heterogeneous solution. It is diluted 100 times and injected in CE. Surprisingly, the electropherogram which is obtained, showed two peaks only. The first peak at 1.21 min is the chloride ion, the second at 1.36 min is the tartarate ion (Fig. 1). No other organic or inorganic cation was detected even at longer migration time. At pH 5, monosaccharides could not be ionized, and as a consequence were not detected [10]. Therefore, from such a complex mixture, CE associated to indirect UV detection allow the detection of two compounds only.

Every day, two calibration curves were done using area (A)=f[concentration (C)] or area/migration time (A/T_m)=f[concentration]. Table 1 shows that the relative standard deviation (RSD) of the slopes of the curves are inferior to 0.23% for the $A=f[C]$ curve and 0.15% for the $A/T_m=f[C]$ curve. The last curve gives better results than the $A=f[C]$ curve.

The intra-day repeatability was tested by preparing five solutions the same day, each using 50 mg of the same raw-powder lot. Each of the four raw-powder lots were screened. Table 2 shows that the results which were obtained with the two calibration curves are very close. The results of three consecutive analysis of the same raw-powder preparation allow calculation of the RSD of the CE analysis, which is 0.6% ($n=15$). The results of the analysis, five preparations of each of the four raw-powder lot, injected three times, gives an RSD inferior to 4%. We chose to keep the $A/T_m=f[C]$ curve to complete our work.

The recovery was determined by adding exactly 5.1, 10.0, 14.9, 20.2 mg of tartaric acid at 50 mg of raw powder. The mixture is treated as described in the Material and methods section. Table 3 shows the results on sample 3. Recoveries, which are close to 100%, indicate that the analysis protocol is correct.

The inter-day repeatability of the method was tested by comparing the results obtained each day during 3 days with a preparation of the samples each day (data not shown). The results, which show an RSD inferior to 4%, are in agreement with the results

Table 2
Quantification of raw calcium tartarate powder

Calibration curve	$A=f[C]$		$A/T_m=f[C]$	
Sample	Tartarate grade (g/g)	RSD (%)[a] ($n=5$)	Tartarate grade (g/g)	RSD (%)[a] ($n=5$)
1	0.4727	1.70	0.4818	1.58
2	0.4808	3.97	0.4833	3.98
3	0.5087	1.03	0.5099	0.95
4	0.5237	1.58	0.5258	1.14

[a] Each analysis was done three times.

Table 3
Recovery of know quantities of tartaric acid added to the sample 3

Calibration curve $A/T_m = f[T_m]$			
Tartaric acid grade (g/g) (theoretical)	Tartaric acid grade (g/g) (experimental)	RSD (%)	Recovery (%)
	0.5087	1.03	
0.6063	0.6167	0.15	101.72
0.7045	0.7205	0.49	102.27
0.8055	0.8348	0.64	103.54
0.9051	0.9054	0.25	100.03

of intra-day repeatability. When the three same samples are analyzed without any new preparation during the 3 days, the RSD is not as good and the results indicate a slight decrease of the concentration of tartaric acid.

The reproducibility inter-person was also tested and two different experimenters were chosen to do this work. The results are shown in Table 4. The RSDs are below 3.2%, which indicates a good ruggedness of our method.

To estimate the precision of our method, we compared results obtained between our laboratory (using CE) and another laboratory (using HPLC). We obtained a good correlation between the values measured with our CE method and the HPLC method [7]. The correlation equation is $y_{(CE)} = 1.0737x_{(HPLC)} - 1.8066$ and $R^2 = 0.9874$.

Table 4
Reproducibility inter-person of tartarate quantification

$A/T_m = f(C)$		
Sample	Tartarate grade (g/g)	RSD (%)
1	0.4800	3.04
2	0.4820	3.18
3	0.5212	1.95

In conclusion, we offer an innovative and quick method to quantify tartaric acid in raw calcium tartarate powder. It uses the same protocol of dissolution of the powder than the previous studies, but quantification of tartaric acid. is realized using CE. The analytical results show the good ruggedness of this method.

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