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Determination of 2,4,6-trichloroanisole by cyclic voltammetry

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Abstract

The electrochemical reduction of 2,4,6-trichloroanisole (TCA), a chlorinated arene with electron-donating substituents, was evaluated by cyclic voltammetry (CV). TCA is a major concern for the winery industry since it is related with “cork taint”, a wine defect. The results obtained showed that CV could be used to detect and quantify TCA in standard solutions. Linear relationships could be set between the current amplitude and TCA concentrations (R>0.990) with detection and quantification limits of 0.08 and 0.26 ppm. Although, these preliminary limits are higher than the human sensory threshold (5 ppt in wine), the simplicity of the methodology confers this study a possible role in the development of more efficient and less expensive process for TCA detection in the industry.

Keywords: 2,4,6-Trichloroanisole; Cork taint; Cyclic voltammetry

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1. Introduction

Cork is widely used for wine stoppers. However, “cork taint” is a wine defect related with their use, and usually attributed to the presence of 2,4,6-trichloroanisole (TCA) (Fig. 1) in cork stoppers. TCA is a

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metabolite formed from chlorophenols by natural fungal strains present in the cork [1]. TCA has a low sensory threshold and can migrate from spoilt corks to the wine, which makes its presence in cork a problem, being the economic loss estimated to be 10 billion US dollars worldwide [2].

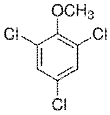


Fig. 1. Structure molecular formula of 2,4,6-trichloroanisole

TCA is usually detected by chromatographic techniques coupled (or not) to solid phase microextraction [3,4], which is beyond the economic possibilities of most cork producers [1]. Lately, immunoanalytical techniques [5-7] were developed and applied allowing the detection of TCA, although in ranges well above the human detection threshold for wine. More recently, Varelas et al. [1] proposed a fast and low-cost biosensor to monitor low TCA concentrations (1-12 ng/l). Nevertheless, the development of more simple analytical procedures to quantify TCA is still a challenging task from both academic and industrial point of view. So, in this work, the use of CV for detecting and quantifying TCA was evaluated.

2. Materials and methods

2.1. Reagents

All treagents were of analytical grade and used as purchased. Acetonitrile (ACN, from Labscan), with a minimum purity of 99.8%, was supplied by Merck. 2,4,6-Trichloroanisole (TCA) and tetrabutylammonium perchlorate (TBAP) were purchased to Aldrich and Fluka, respectively, both with a minimum purity of 99%.

2.2. Voltammetric system and measurements

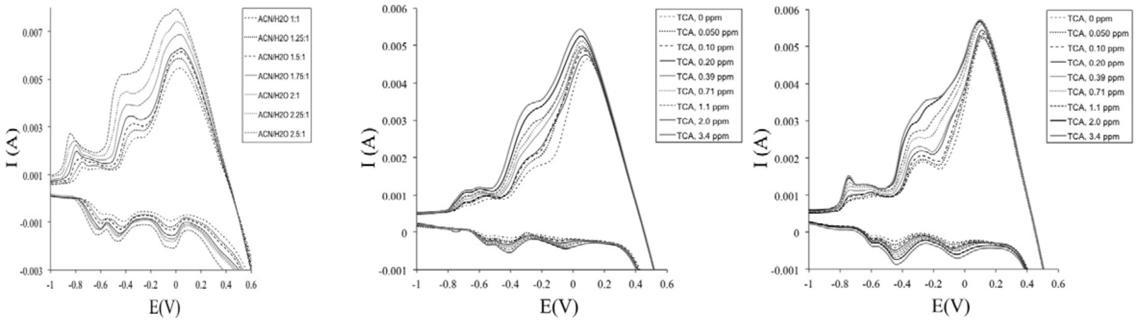
A silver working electrode (M295Ag, Radiometer), a platinum counter electrode (M241Pt, Radiometer) and an Ag/AgCl double–junction reference electrode (M90-02, Orion), were connected to a Potentiostat-Galvanostat device (PG580, Uniscan). UiEChem v.1.34 software (Unisann Instruments Ltd), installed in a PC computer, was used to acquire the signals profiles.

Standard TCA solutions (0.05 to 100 ppm) were prepared by dissolving pre-weighted known amounts of TCA in ACN/water solutions with 0.1 M of TBAP, followed by appropriate dilutions. Several mixtures of ACN/water with different volumetric proportions were used (1:1 to 2.5:1 v:v, of ACN/water, respectively). Voltamograms were recorded between -2.0 and 1.6 V, at a potential scan rate of 100 mV/s. For each measurement, two scans were performed, corresponding to a total time of analysis lower than 2 minutes. The standard addition method was used to calibrate the system for TCA quantification. For this purpose several solutions of TCA in 0.1 M TBAP ACN/water (1:1 or 1.5:1 v/v), with concentrations ranging from 0.05 to 100 ppm, were used. The detection and quantification limits were determined from the parameters of the calibration curve, being defined as 3.3 and 10 times the value of the intercept error divided by the slope, respectively [8,9].

3. Results and discussion

The performance of a CV device coupled with a Ag working electrode, a Pt counter electrode and a Ag/AgCl reference electrode, to detect and quantify TCA concentration in 0.1 M TBAP ACN/water standard solutions, was evaluated. First, the possible influence of the solvent composition in the voltammetric signal profiles was investigated. Voltamograms of a standard solution of TCA (10 ppm) in several 0.1 M TBAP ACN/water mixtures (from 1:1 up to 2.5:1 v/v) were recorded between -2.0 and 1.6 V, at a potential scan rate of 100 mV/s. The cyclic voltammetric signal profiles obtained showed that the relative amount of acetronitrile in the aqueous solvent mixture affects the intensity of the voltammetric signals recorded, showing a tendency of increasing the signal. These preliminary results pointed out that the selection of an appropriate solvent may be a key point. Although higher ACN proportions allowed obtaining a better and more precise signal (Fig. 2a), taking into account the objective of developing a low-cost procedure to detect and quantify TCA, in this work two ACN/water mixtures were selected, namely 1:1 and 1.5:1 (v:v).

For each solvent mixture selected (1:1 or 1.5:1 ACN/water with 0.1 M of TBAP; v:v) the effect of increasing concentrations of TCA on the cathodic and anodic profiles were evaluated. Fig. 2b and 2c show the cyclic voltammograms obtained, with an Ag working electrode, of different TCA concentrations, expressed as ppm, for 0.1 M of TBAP in ACN/water (1:1 and 1.5:1; v:v), recorded at a potential scan rate of 100 mV/s. The profiles recorded show, in general, an increasing voltammetric signal with increasing TCA concentrations, in both cathodic and anodic regions.



(a) (b) (c)

Fig. 2. Cyclic voltammograms obtained: (a) for 10 ppm of TCA in mixtures of 0.1 M of TBAP ACN/water with different ACN amounts; (b) for increasing concentration of TCA in 0.1 M of TBAP in ACN/water mixture (1:1; v:v); (c) for increasing concentration of TCA in 0.1 M of TBAP in ACN/water mixture (1.5:1; v:v)

Two linear calibration curves could be established (one for each solvent mixture) relating the normalized amplitude of the current intensity (obtained by subtracting the solvent effect) and TCA concentrations. The parameters of the linear regression calibration curves are given in Table 1, as well as the respective LOD and LOQ values.

Table 1. TCA standard addition calibration curves for two ACN/water mixtures of 0.1 M TBAP solvent.

ACN/water proportion	TCA concentration range (ppm)	n[a]	Slope[b] (mA/ppm)	Intercept[b] (mA)	R[c]	LOD[d] (ppm)	LOQ[e] (ppm)
1:1 (v:v)	0.05-0.71	4	0.0125 (±0.0008)	0.0058 (±0.0003)	0.9960	0.08	0.26
1.5:1 (v:v)	0.10-1.13	5	0.013 (±0.001)	0.0044 (±0.0006)	0.9913	0.16	0.48

[a] Number of points considered for the regression.

[b] Standard deviation of the slope and intercept of the regression line are given in parentheses

[c] Correlation coefficient; [d] Limit of detection; [e] Limit of quantification

The low theoretical LOD and LOQ values obtained in this preliminary work, where commercial electrodes were used as purchased, without any modification or treatment, although still being higher than the sensory threshold (1-10 ppt), allow envisaging the future practical application of this simple, fast and low-cost methodology.

4. Conclusions

The results achieved in this work showed that the lowest LOD and LOQ values were obtained with the aqueous solvent mixture containing the lower ACN amount. On the other hand, they also show that increasing the ACN proportion in the solvent mixture allows obtaining more defined and greater signals.

Therefore, although these preliminary results show the feasibility of the CV system for TCA analysis, when compared with other immunoanalytical techniques recently described, further work is required to:

- Reduce detection and quantification analytical limits
- Select the best solvent composition (ACN vs water proportion)
- Infer about the best concentration of TBAP in the solvent solution
- Study the possibility of modifying the commercial electrodes

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