

# Selective Separation of Organic Oxyacids from Aqueous Phase by Reactive Extraction

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## Abstracts

*The paper deals with the study of the extraction mechanism of tartaric acid from the aqueous phase using Amberlite LA-2 butyl acetate mixture. A method of selective separation of tartaric, apple and citric acid is proposed. Reactive extraction has been achieved in a volume proportion of 1:1. In order, to provide a rapid separation of the emulsion and an increase in the efficiency of the extraction process, octanol-1 has been added to the organic solvent.*

**Keywords:** *secondary wine products, tartaric acid, organic oxyacids, reactive extraction, Amberlite LA-2.*

## Introduction

Rational processing of particular secondary wine products (wine yeast, tartar, squeezing, distiller's wash resulting from raw wine distillation, etc.) allows to receive valorous products for a number of industries of the national economy. One of this wide used products is the tartaric (+) acid. In the industry, the main source of tartaric acid is the potassium acid salt named tartar, which given a low solubility in diluted alcohol precipitates together with wine yeast upon the end of the fermentation process [1].

The tartaric acid is used in the food industry as an additive in jam and fruit jelly (3g/kg), in cacao powder (5 g/kg), in mayonnaise (5g/kg), in tomato concentrate in order to maintain the pH value of 4,3, in tinned pear, strawberry, etc.; it is used for the acidification of young wine, liquor, etc. □2□; in bread manufacturing, pharmaceutical industry, photochemical industry, it is also used for fabric dyeing to ensure a long endurance of the color, in metal surfaces' coating, as a reagent in various chemical analyses.

The tartaric acid and its compounds may be substituted in the industry with other organic oxyacids (citric, apple), but it may not be substituted in the electro-technical industry. Given its pyro- and piezoelectric properties, ability to form electrostatic field and echo backgrounds the tartaric compounds are widely used in this area [3].

Already-existing technologies of receiving the tartaric acid from secondary wine products consist in a number of complicated material- and energy-consuming technological procedures. The main stages of the separation of the tartaric acid from wine wastes are: the dissolution of tartaric compounds ( $\text{KHC}_4\text{H}_4\text{O}_6$ ,  $\text{CaC}_4\text{H}_4\text{O}_6$ ), precipitation in the form of calcium compounds of tartaric acids and its release with the use of mineral acid, followed by a number of solution concentration and crystallization processes of final products [3, 4, 5]. The elaboration of new technologies for the production of tartaric acid from secondary wine products, using the reactive extraction, would represent quite an advantageous procedure with a much smaller material- and energy consumption in comparison with already-existing technologies and a lower final product cost.

Reactive extraction of organic compounds is now being industrially used for the recovery of particular toxic derivatives from waste waters, for the separation of some biologically active products from fermentation liquids, for purification by selective separation of some acid composites etc.

## **Materials and Methods**

### **Reagents**

In order to obtain the exact data in the proposed experiment there have been used high purity reagents and exact specific methods of organic extracts' dosage, titration and spectrophotometric methods accordingly.

Amberlite LA-2 *Sigma-Aldrich* (Steinheim, Germany), butyl acetate *Merck* (Darmstadt, Germany), octanol – 1 *Merck* (Schuchardt, Germany), (+) – tartaric acid *Reahim* (Ural, Russia), apple acid *Merck* (Schuchardt, Germany), citric acid *Merck* (Schuchardt, Germany), sodium metavanadate *Reahim* (Ural, Russia), glacial acetic acid *Reactivul* (Bucharest, Romania), sodium hydroxide *Chemapol* (Prahá, Czechoslovakia), phenolphthalein *Reactivul* (Bucharest, Romania) were used.

### **Apparatus**

An extraction device and the MLW T23D centrifugal separator have been used in order to extract tartaric acid from aqueous phase. The colorimetry assays were made by means of the Spectromom 410 VIS spectrophotometer.

### **Procedure**

Reactive extraction installation comprises a glass column with an interior diameter of 37 mm and 240 mm height, provided with a vibrating agitator that permits an intensive

agitation of the two phases. The vibrating agitator consists of a perforated disk with a diameter of 45 mm and a free section of 17%. Vibrations have been generated by a 50 Hz frequency and an amplitude in the limits of 0 – 4 mm. The resulting emulsion has been evacuated from the inferior part of the column and separated in a centrifuge separator at a 2500 rot/min rate.

This experimental study consists in the selective separation of particular organic oxyacids from the solution that results from tartaric compounds' dissolution from secondary wine products with the use of the method of reactive extraction. To this end, a specific extraction mechanism for the tartaric acid has been developed and then based on the preliminary data of the experiment □6□ a selective extraction of apple and citric acids from initial aqueous phase has been done.

To study the individual extraction of tartaric acid, aqueous phases have been used with the following initial concentrations: 0,5 – 50 g/l. Reactive extraction has been realized with a 42 g/l solution of Amberlite LA-2 butyl acetate mixture. To raise the efficiency of the reactive extraction, octanol-1 has been added to the solution as a phase modifier.

Oxyacid selective separation has been studied on different aqueous phases containing composites of tartar, apple and citric acids, maintaining the final proportion of these components in tartaric compounds dissolution from secondary wine products. Data from Babo and Mach has been considered (**Table 1**), accordingly: tartaric acid is obtained in a concentration of 1,7 - 4,8 g/l (from wine yeast) and of 6,8 – 7,6 g/l (from tartar) and represents 70 – 95% from the total content of organic oxyacids.

So, in a number of determinations there has been maintained a constant concentration of tartaric acid (5 g/l), and the concentration of the apple and citric acids has been kept within the limits of 0,5 – 4 g/l.

Then a solution with a constant composition of tartaric acid (5 g/l), apple acid (2 g/l) and citric acid (0,25 g/l) has been used, as the concentration of Amberlite LA-2 butyl acetate mixture varied in the limits of 0 – 50 g/l.

The reactive extraction has been achieved using a volume proportion between aqueous and organic phases equal to 1:1, working with 25 ml samples of every phase. The time of extraction consisted in 1 minute.

The progress of the extraction has been followed by the quantitative analysis of the tartaric acid in the aqueous phase using the spectrophotometric method, measuring the colored compound's absorption with sodium metavanadate (5% aqueous solution) in an acid medium (acid acetic glacial) with the use of VIZ spectrophotometer (Spectromom 410) at 525 nm and measuring (by titration) the total oxyacid content with NaOH (0,05 n) in the presence of phenolphthalein (0,1% alcohol solution).

The reactive extraction efficiency has been calculated with the expression:

$$Y = (1 - C_{ar} / C_a) \times 100 \% \quad (1)$$

where Y – the reactive extraction efficiency;

$C_{ar}$  – tartaric acid concentration in refined solution, g/l;

$C_a$  – initial tartaric acid concentration in aqueous phase, g/l.

Theoretic extraction efficiencies of the proposed mechanisms, have been calculated exactly as the experimental ones, though implying a complete reaction between the extract and oxyacids.

## Results and Discussions

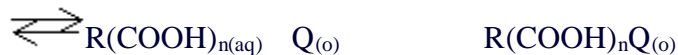
The general inter-phase equilibrium that is established in the reaction between organic oxyacids and Amberlite LA-2 is the following:



where  $R(\text{COOH})_n$  represents the oxyacid, accordingly  $n=2$  for tartaric and apple acids,  $n = 3$  for citric acid, and Q – Amberlite LA-2.

Depending on the molar ratio between the components, organic oxyacid and extraction agent, three types of chemical inter-phase reactions used for reactive extraction may be distinguished:

a) In the case of  $m : p$  proportion close to 1, the organic oxyacid and the extraction agent form the hydrophobic complex in a equimolar proportion:



b) In the case of molar proportions between the carboxylic acid and the extraction agent much lower than 1 ( $m:p \ll 1$ ), reactive extraction results in the formation of particular complexes  $R(\text{COOH})_n Q_n$  in the organic phase:



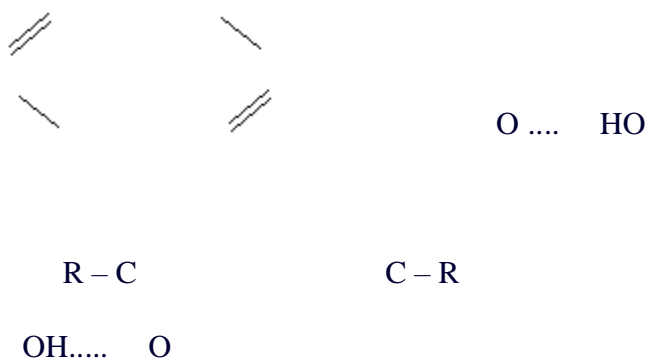
c) In the case of reactive extraction in nonpolar solvents (for example butyl acetate) of existent high initial concentrations of oxyacids in aqueous solutions, a third phase is possible to appear, representing a stable emulsion, with a high content of acid complexes, insoluble in aqueous phase as well as in the organic one:



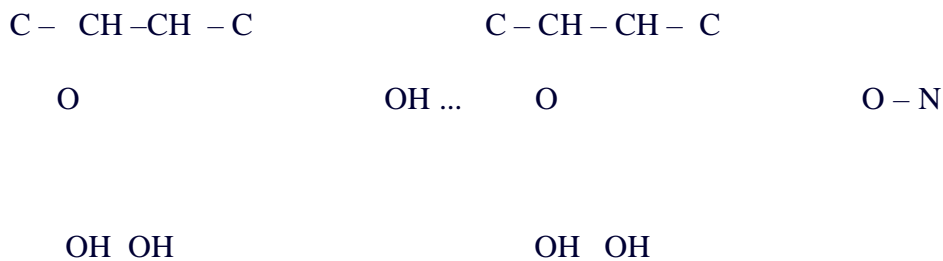
For a more rapid separation of the emulsion that results from the third phase, a phase modifier is being added to the organic solvent, representing a long chain aliphatic alcohol, a component assuring a higher solubility of the acid complex in the extract phase [7].

The mechanism of individual tartaric acid reactive extraction has been studied varying the concentration in aqueous solution. The produced results have been compared to theoretical values corresponding to possible extraction mechanisms a,b,c (Figure 1).

Analysis of the individual mechanism of tartaric acid reactive extraction shows that at concentrations lower than 7,6 g/l the reactive extraction takes place according to mechanism **b** ( $R(COOH)_2Q_2$ ). At the rise of tartaric acid concentration there establishes an intermediate mechanism between theoretic mechanisms **a** and **b**. This phenomena may be explained by formation of tartaric acid specific dimmers.



Accordingly, one molecules of Amberlite LA -2 extracts more than one molecule of tartaric acid as resulted from amine aduct structure - tartaric acid partially dimerized:



Using the results of experiment [6] a comparative variation of tartaric, apple and citric acids reactive extraction efficiency may be observed (Figure 2).

Irrespective of acid nature, it may be stated that at low concentrations reactive extraction takes place according to mechanism **b**. Maximum acid concentrations at which extraction mechanism **b** takes place are the following: tartaric acid - 7,6 g/l, citric acid- 17,0 g/l, apple acid - 17,4 g/l.

Addition of octanol-1 to the organic phase in the case of tartaric acid extraction resulted in a rapid phase separation increasing the extraction grade by 3 - 7 % (figure1).

For successful oxyacids selective extraction a difference in extraction grades, as a result of difference in concentrations, will represent a necessary condition.

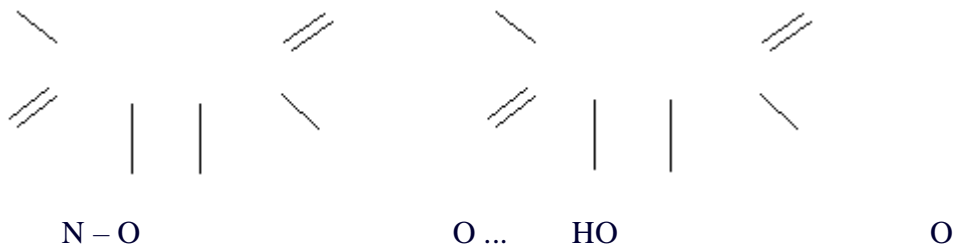
To define the conditions of selective extraction, the experimental study has been continued with the analysis of variation of tartaric acid extraction efficiency, on one hand, and of the global secondary acids extraction efficiency, on the other hand, maintaining the initial tartaric acid concentration. 25 ml of solution with initial concentrations of 5 g/l of tartaric acid and accordingly 0,5 – 4 g/l apple and citric acids have been subjected to extraction with 25 ml of Amberlite LA-2 (20 g/l) in butyl acetate. The produced curves are showed on (Figure 3).

Figure 3 shows that at low concentrations of secondary acids (0,5 g/l) the tartaric acid extraction efficiency is 82,2%, and that of the secondary acids - 7%. At the same time at a total concentration of secondary acids equal to 2 g/l the tartaric acid and apple and citric acids extraction efficiency consists of approximately - 72 %. Thus, the rise in secondary acids concentration determines not only the efficiency of their extraction, but also the tartaric acid extraction efficiency.

Keeping the acids proportion that results from the tartaric compounds dissolution from secondary wine products, the influence of extraction agent concentration over the efficiency of tartaric acid extraction, as well as of the secondary acids has been studied. 25 ml solution containing 5 g/l tartaric acid, 2 g/l apple and 0,25 g/l citric acids have been subjected to extraction with 25 ml butyl acetate containing accordingly 0 – 50 g/l of Amberlite LA-2. The produced curves are shown on (Figure 4). The selectivity of the extraction process is shown in (Figure 5).

Figure 5 shows that in the area of low concentration of the extraction reagent (Amberlite LA-2) the secondary acids extraction efficiency is quite high, while that of the tartaric acid is low. The secondary acids extraction efficiency is 97,34 % and 3,12 % for tartaric acid when using butyl acetate containing 7,5 g/l of Amberlite LA-2.

To study the influence of octanol –1 on the selectivity of acids separation a solution has been extracted with an initial tartaric acid concentration of 5 g/l and a total concentration of apple and citric acids equal to 2,25 g/l with butyl acetate containing 7,5 g/l of Amberlite LA-2, obtaining a rise in the secondary acids extraction efficiency from 97,34% to 99,75%, with simultaneous decrease in tartaric acid extraction efficiency from 3,12% to 2,08%.

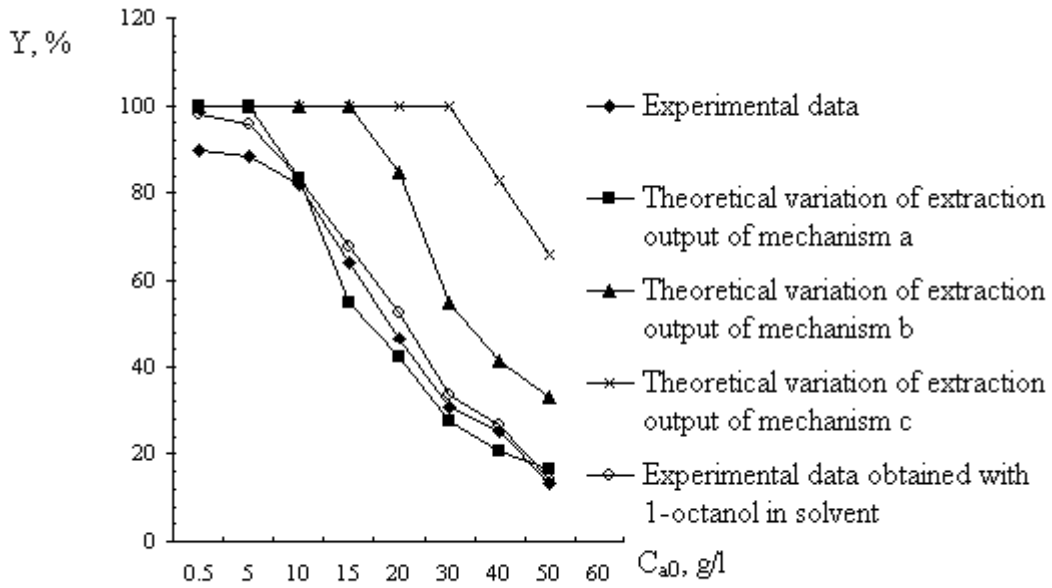


## Conclusions

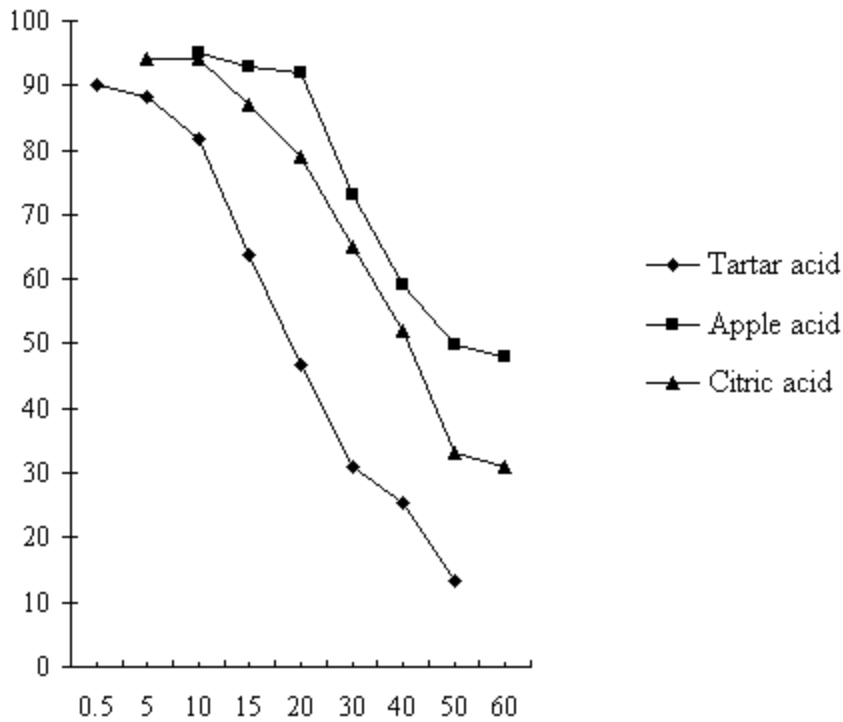
The experimental data have shown the possibility of selective separation using reactive extraction of apple and citric acids from aqueous phase with a simultaneous presence of tartaric acid. The main condition of selective separation is maintenance of the molar ratio between organic oxyacids and Amberlite LA-2 equal to 1. The efficiency of selective separation rises after the addition of a phase modifier, octanol-1, which raises the phase separation rate and the difference between the efficiencies of tartaric acids extraction and those of secondary acids (apple and citric acids). Using this method secondary acids are eliminated from the liquid that results from tartaric compounds dissolution from secondary wine products; single tartaric acid remaining in the solution is easily extracted with butyl acetate containing 60-70 g/l of Amberlite LA-2. It suggests a much more advantageous method of obtaining the tartaric acid from vinous wastes than the existing ones. As a result of amine regeneration tartaric acid of high purity may be produced and at the same time secondary acids may be recovered.

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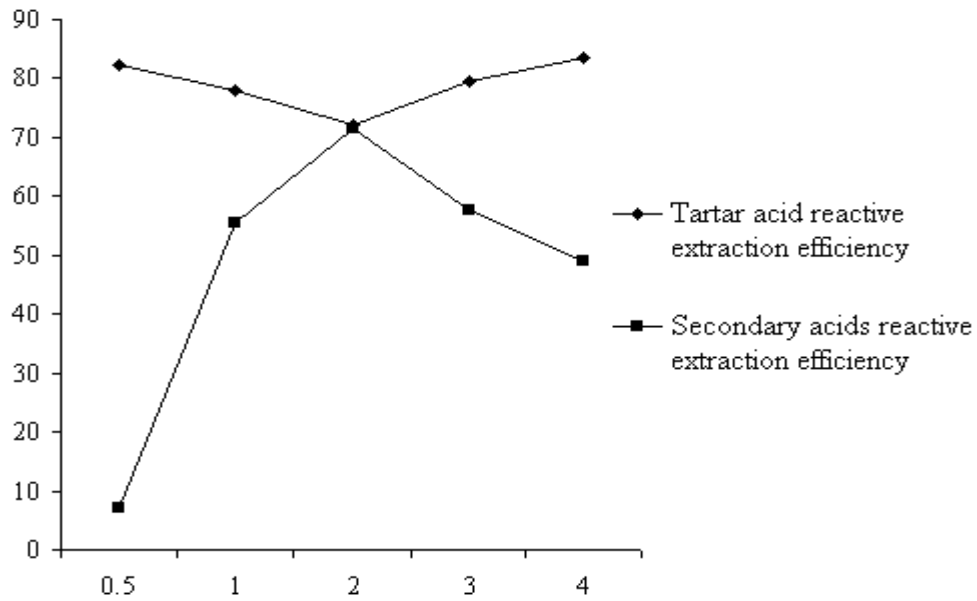


**Figure 1.** Variation of the tartaric acid reactive extraction efficiency with its concentration in aqueous phase.

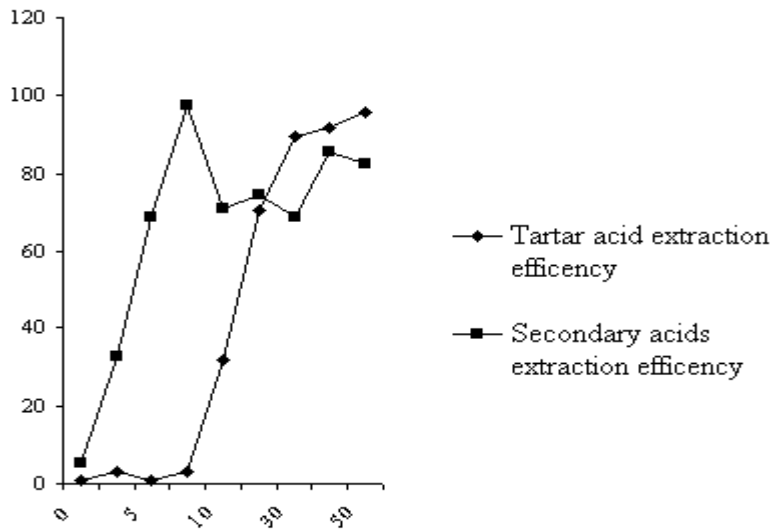


**Figure 2.** Comparative variation of tartaric, apple and citric acids reactive concentration efficiency.

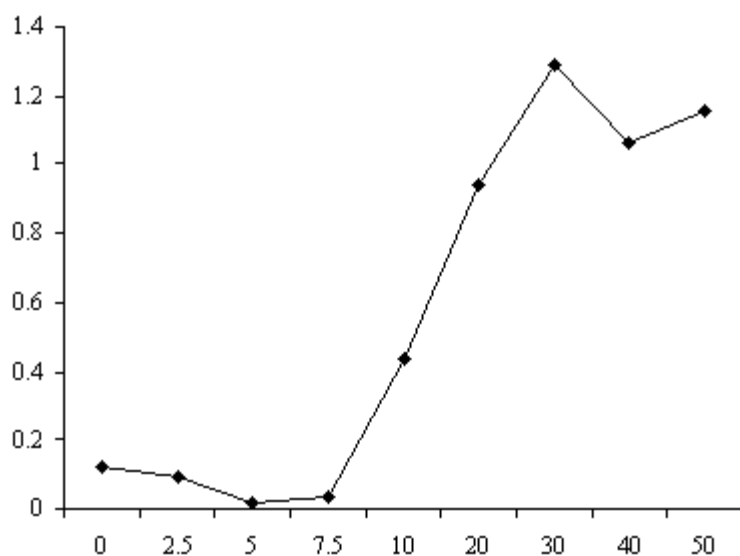




**Figure 3.** Variation of extraction efficiency with the total initial concentration of apple and citric acids ( $C_a$  tartaric acid = 5 g/l).



**Figure 4.** Variation of extraction efficiency with the concentration of the extraction reagent.



**Figure 5.** Variation of selectivity with extraction agent concentration.

**Table 1.** Some acids composition in must and wine.

Oxyacid	Composition in must, g /l	Composition in wine, g /l
Tartaric acid	1 – 8	0,4 – 5,6
Apple acid	1 – 20	0 – 0,8
Lactic acid	0	0 – 7
Citric acid	Very low	Very low
Amber acid	0	0,2 – 0,8
Acetic acid	Traces	0,2 – 0,8