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SIMULTANEOUS DETERMINATION OF TARTARIC ACID AND POTASSIUM IN WINES USING A DIALYSIS MULTICOMMUTED FLOW SYSTEM

Introduction

- Development of a multicommuted flow system ⇨ recirculation of the solutions
  - reduction of reagents consumption and waste generation
  - tartaric acid (TA) determination by spectrophotometry
  - potassium determination by potentiometry
- In-line dilution and minimization of matrix effects
  - introduction of a dialysis device
- Application of the method to table and Port wines
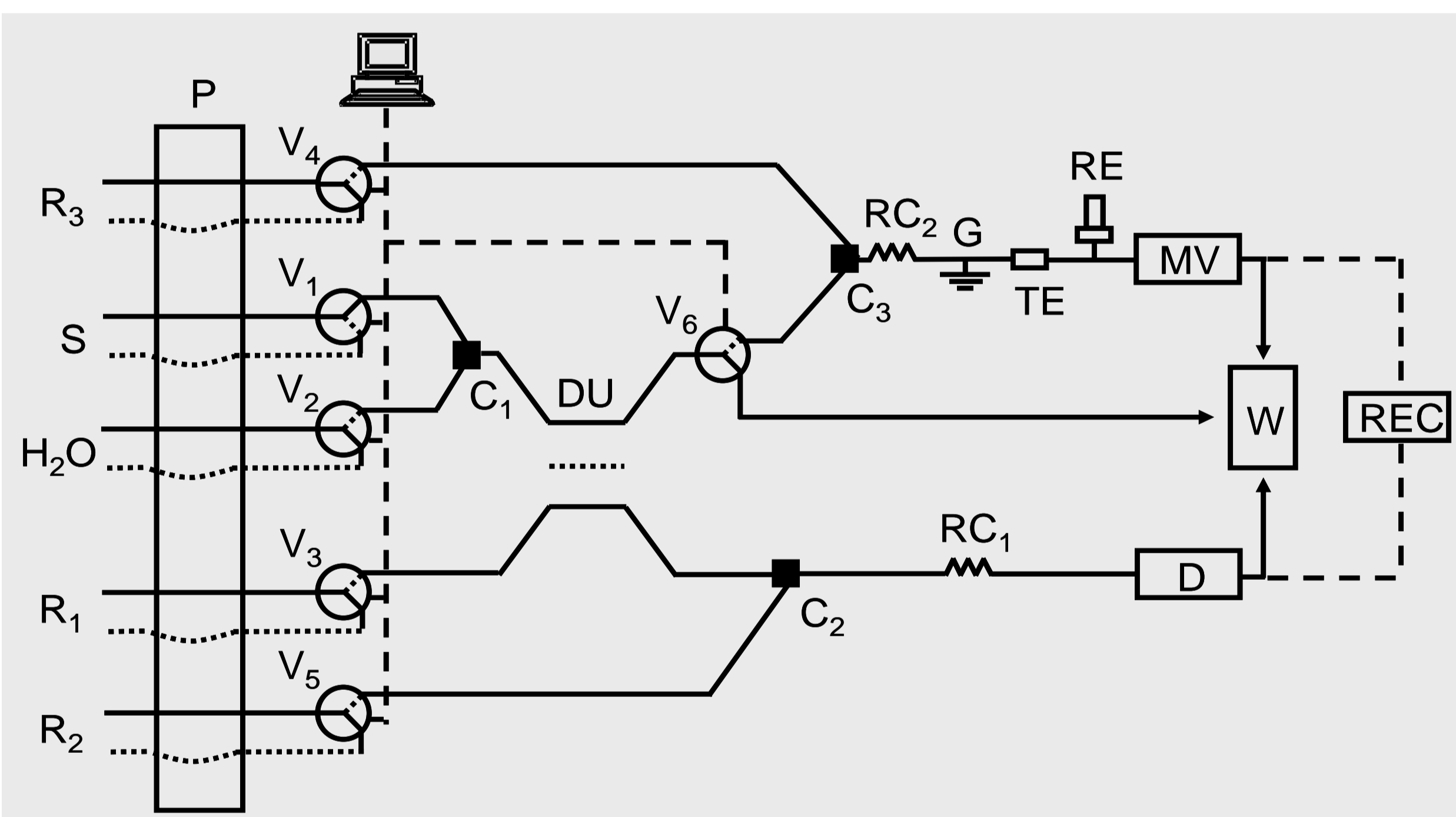
Manifold and protocol sequence

Figure 1. Schematic diagram of the multicommuted flow system P: peristaltic pump; V_i: solenoid valves; C_i: confluences; DU: dialysis unit; RC_i: reaction coils: RC_1 = 200 cm; RC_2 = 25 cm; S: sample, 0.56 mL min^{-1}; H_2O, 0.56 mL min^{-1}; R_1: acetic acid, 0.56 mL min^{-1}; R_2: vanadate colorimetric reagent 0.56 mL min^{-1}; R_3: ionic strength adjuster solution, 1.4 mL min^{-1}; W: waste. D: spectrophotometer (500 nm); G: ground electrode; TE: tubular ion selective electrode; RE: reference electrode; MV: voltmeter; REC: dual channel chart recorder. In the valves, the position "on" is represented by a continuous line and the position "off" is represented by a dotted line.

Step	Description	Position of the commutation valves						Time (s)
		V_1	V_2	V_3	V_4	V_5	V_6	
1	Wash connection between V_1 and C_1 with sample	N	F	F	N	F	N	15
2	Wash connection between C_1 and V_6 with H_2O	F	F	F	N	F	N	20
3	Sample introduction	N	N	F	F	F	N	42.9
4	Propel towards the detectors; signal registration	F	F	F	F	F	F	80

The letters N and F correspond to positions "on" and "off" of the commutation valves, respectively
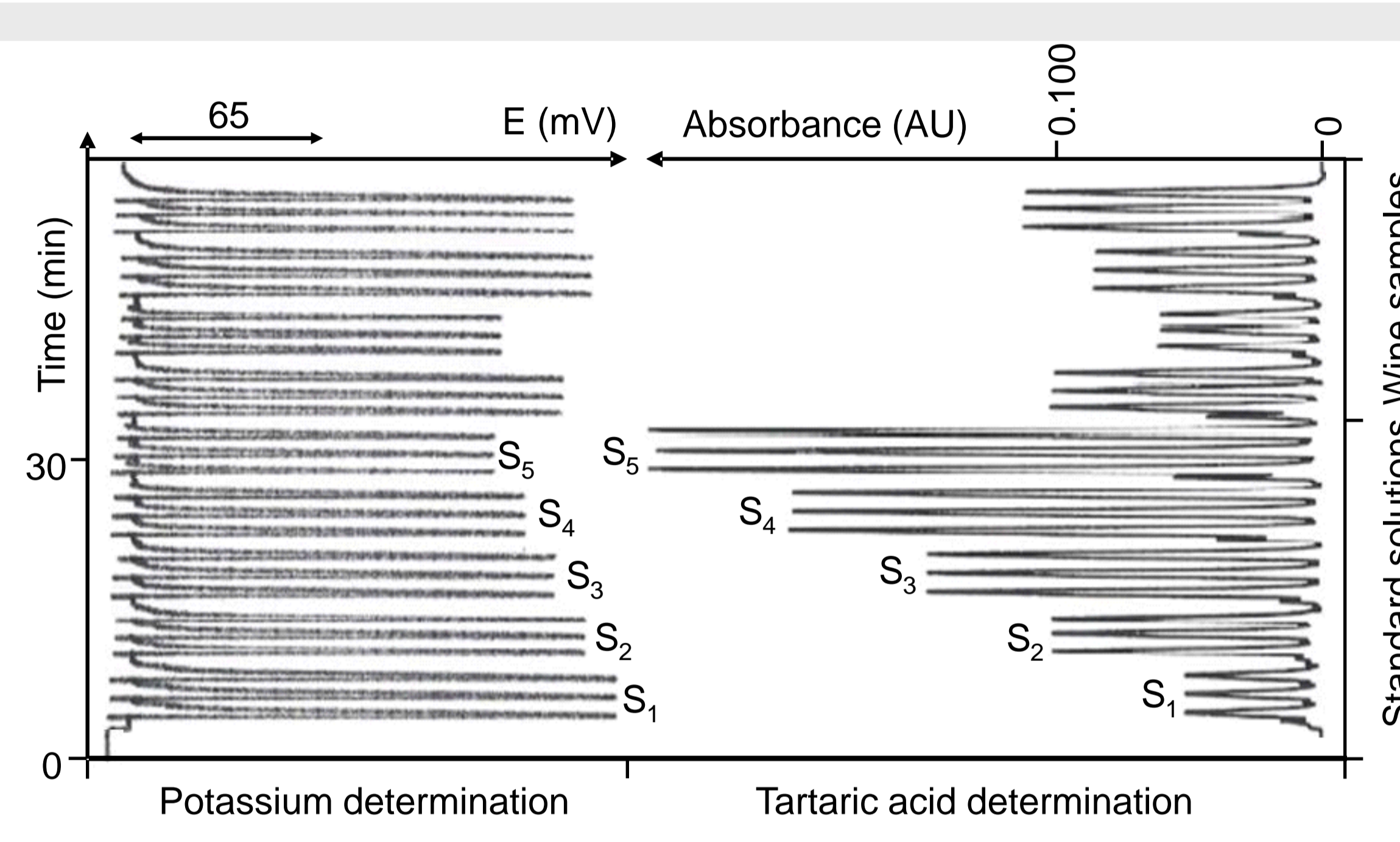
Calibration curve and analysis of table wines

Figure 2. Recorder output obtained by the presented methodology in the determination of table wines, corresponding to the analysis of a set of standard solutions prepared in ethanol 12% (S_1 = tartaric acid (TA) 1.00 g L^{-1} + K$^+$ 2000 mg L^{-1}; S_2 = TA 2.00 g L^{-1} + K$^+$ 1290 mg L^{-1}; S_3 = TA 3.00 g L^{-1} + K$^+$ 860 mg L^{-1}; S_4 = TA 4.00 g L^{-1} + K$^+$ 590 mg L^{-1}; S_5 = TA 5.00 g L^{-1} + K$^+$ 390 mg L^{-1}) and four different table wine samples.

Interference study

Species studied	Concentration tested (g L^{-1})	Relative deviation (%)	
		Tartaric acid determination	Potassium determination
Glucose	10	-0.91[a] -1.38[b]	-0.65[a] -3.48[b]
Fructose	10	-1.21[a] -2.68[b]	-2.60[a] -2.89[b]
Citric acid	1	-0.92[a] 0.66[b]	-1.59[a] 0.37[b]
Ascorbic acid	0.15	-4.54[a] -4.95[b]	1.65[a] 0.98[b]
Lactic acid	2	-3.68[a] 2.64[b]	0.67[a] 3.66[b]
Malic acid	2[a] 1.5[b]	-4.39[a] -3.54[b]	0.36[a] -2.61[b]
Acetic acid	5	-1.51[a] 0.69[b]	-1.95[a] 1.00[b]
CO_2	2	4.19[a] n.d.[b]	-0.64[a] n.d.[b]
SO_2	0.25	0.31[a] 1.38[b]	1.00[a] 3.74[b]
Glycerol	10	-0.92[a] 1.31[b]	-0.91[a] 2.96[b]

[a]Table wines; [b]Port wines; nd – not determined

Application to wine samples

Parameters of the equation $C_s = C_0 + SC_r$ for comparison of the results (g L^{-1} of TA; mg L^{-1} of K$^+$) obtained by the developed method (C_s) and the manual procedures (C_r), and values of the relative standard deviation (R.S.D.) obtained from 10 consecutive analysis of 2 wine samples, for each wine type.

	Sample	$C_0{}^a$	S^a	R^b	R.S.D.^{c} (%)
TA	white table wines n = 10	-0.025 (±0.181)	1.02 (±0.11)	0.992	0.72 (1.2) 0.37 (2.2)
	red table wines n = 10	0.056 (±0.384)	0.97 (±0.20)	0.969	1.0 (1.8) 0.77 (2.4)
	Port wines n = 10	-0.071 (±0.086)	1.09 (±0.10)	0.994	2.1 (0.71) 1.8 (1.1)
	All wines n = 30	-0.005 (±0.056)	1.01 (±0.04)	0.996	
K$^+$	white table wines n = 10	12.4 (±57.9)	0.977 (±0.079)	0.995	2.4 (395) 1.1 (1068)
	red table wines n = 10	28.8 (±270.7)	0.973 (±0.242)	0.956	2.2 (1258) 2.1 (978)
	Port wines n = 10	61.4 (±149.1)	0.911 (±0.187)	0.970	1.7 (711) 2.1 (899)
	All wines n = 30	0.4 (±37.8)	0.994 (±0.042)	0.994	

^{a}The values in parentheses are the limits of the 95% confidence intervals for the estimated parameters; ^{b}Correlation coefficient; ^{c}The values in parentheses are the tested sample concentrations, expressed in g L^{-1} of tartaric acid and mg L^{-1} of potassium

Conclusions

- Dialysis separation device ⇨ analysis of both analytes without any sample treatment, using the same sample plug in a single manifold
- Simple and inexpensive instrumentation, easy manipulation and high determination throughput (52 h^{-1})
- Good accuracy and precision
- Results obtained by the developed system compared well with those provided by the manual methods
- Useful to assess wine stability

Acknowledgements