

Application Bulletin

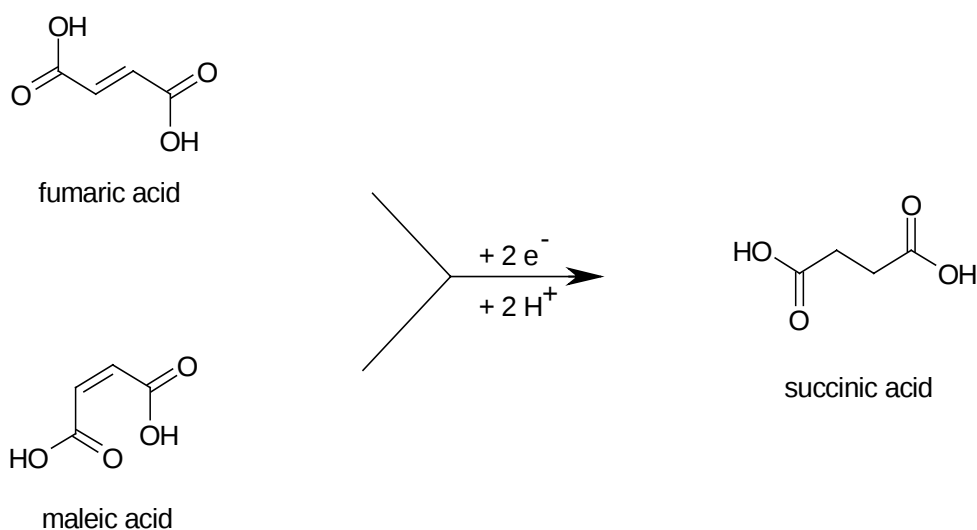
Of interest to: General analytical laboratories, Foodstuffs, Plastics

B 1, 6, 7

Polarographic determination of maleic and fumaric acid alone or in mixtures

Summary

Maleic and fumaric acid can be reduced electrochemically to succinic acid. In acidic solutions a differentiation of the two acids is not possible since both are reduced at the same potential. On the other hand, separation at pH 7.8 ... 8.0 is easily possible since fumaric acid is now more difficult to reduce at the lower proton concentration (as a result of cis-trans isomerism) than maleic acid.



Apparatus and accessories

- 746 VA Trace Analyzer with 747 VA Stand
or
- 757 VA Computrace
- pH-Meter with combined glass electrode

Remarks

- Maleic and fumaric acid are usually easy to determine in the presence of other carboxylic acids, because carboxylic acids without conjugated double bonds are reduced only with difficulty and saturated carboxylic acids not at all. This permits their determination in, e.g. malic acid or in the presence of acrylic acid.

Literature

- Elving P.J., Martin A.J., Rosenthal I.
Polarographic determination of mixtures of maleic and fumaric acid and their dithylesters.
Anal Chem 25, (1953) 1082 - 1084
Ref: Fresenius Z Anal Chem 146, (1955) 122
- Traxton M.E.
Eine Methode zur polarographischen Bestimmung von Malein-, Fumar- und o-Phthalsäure in Polyesterharzen und Weichmachern.
Chem and Ind (1966) 1613 - 1615
Ref: Fresenius Z Anal Chem 232, (1967) 390
- Volodina V.I., Tarasov A.I., Kurbatov D.I.
Polarographische Bestimmung von Fumar-Doppelbindungen in Co-Polymerisaten von ungesättigten Polyestern.
Zh Anal Khim 22, (1967) 1438 - 1439
Ref: Fresenius Z Anal Chem 247, (1969) 122
- Taylor J.R., Blomquist V.H.
Polarographic determination of fumaric acid in food.
J Assoc Off Anal Chem 51/3, (1968) 533 - 537
Ref: Fresenius Z Anal Chem 248, (1969) 109
- Southern Anal. Ltd.
Polarographic determination of maleic and fumaric acid in malic acid.
Appl Advisory Sev 300 P, (1969)
Ref: Fresenius Z Anal Chem 254, (1971) 77

Method 1

Determination of the sum of maleic and fumaric acid

Reagents

All used reagents must be of purest quality possible (p.a. or suprapur). Only high purity water is used to prepare the solutions.

- Hydrochloric acid, suprapur, w(HCl) = 30%
- Fumaric acid, puriss p.a., CAS 110-17-8
- Maleic acid, puriss p.a., CAS 110-16-7

Ready-to-use solutions

- Maleic acid standard solution: $\beta(\text{maleic acid}) = 1 \text{ g/L}$
Dissolve 100 mg maleic acid in dist. water and add 2 mL ammonium buffer. Adjust the pH value to 8.0 with sodium hydroxide and fill up to 100 mL with dist. water.
- Fumaric acid standard solution: $\beta(\text{fumaric acid}) = 1 \text{ g/L}$
Dissolve 100 mg fumaric acid in dist. water and add 2 mL ammonium buffer. Adjust the pH value to 8.0 with sodium hydroxide and fill up to 100 mL with dist. water.

Analysis

Measuring solution:

10 mL (diluted) sample
+ 1 mL HCl

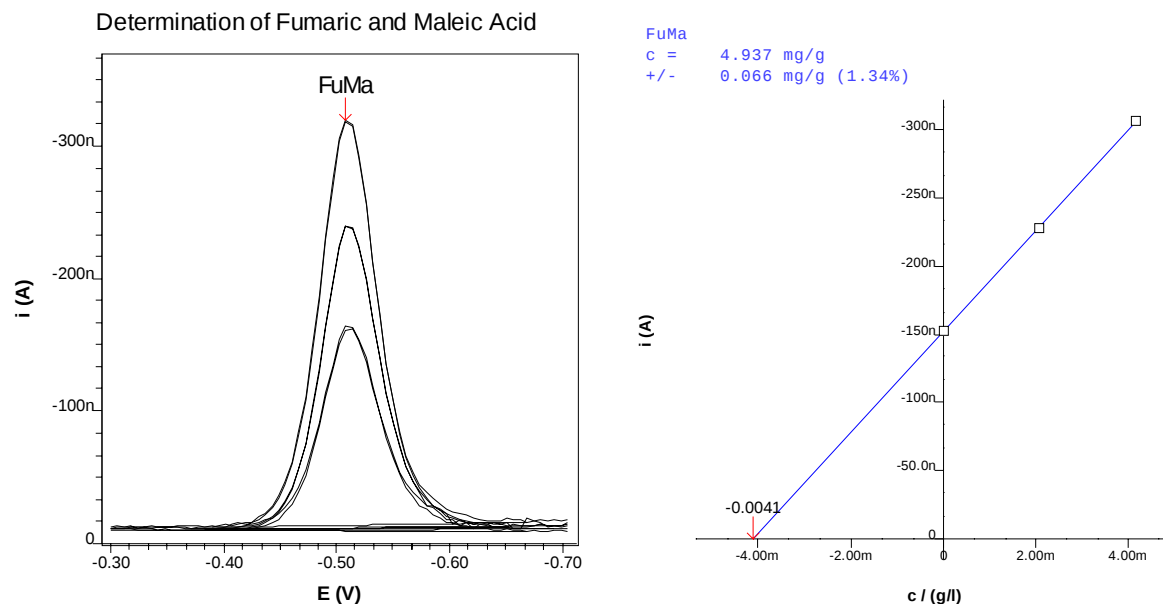
The polarogram is recorded with following parameters:

working electrode	DME
stirrer speed (rpm)	2000
mode	DP
purge time	300 s
equilibration time	5 s
pulse amplitude	25 mV
start potential	-300 mV
end potential	-700 mV
voltage step	6 mV
measure time	20 ms
pulse time	40 ms
voltage step time	0.6 s
sweep rate	10 mV/s
peak potential	-520 mV

The concentration is determined by standard addition.

Example

Determination of the sum of maleic and fumaric acid in malic acid with the 757 VA Computrace
 (1 g malic acid in 100 mL dist. water, 1 mL polarographed; 1. Addition 25 µg fumaric acid, 2. Addition 25 µg maleic acid)



Sample volume 1 g

Results 4.9 mg/g maleic-/fumaric acid

Report

===== METROHM 757 VA COMPUTRACE (5.757.0010) =====							
Determ.	:	10271554_Malic Acid.dth					
Date	:	1999-10-27	Time:		15:54:40		
Modified	:	2001-04-25 10:43:27	User:		Cell volume: 12.000 ml		
Ident					Sample volume 1.000 ml		

Method	:	AB179_Det of Fumaric and Maleic Acid.mth					
Title	:	Determination of Fumaric and Maleic Acid					
Remark1	:	1 mL sample + 10 mL H2O + 1 mL HCl (30 %)					
Remark2	:	1. 25 ug Fumaric Acid / 2. 25 ug Maleic Acid					

Substance	:	FuMa				Comments	
Mass conc.	:	4.114	mg/l			-----	
MC.dev.	:	0.055	mg/l	(	1.34%)		
Mass	:	49.372	ug				
Add.mass	:	25.000	ug				
	VR	V	nA	i.mean	Std.Dev.	i.delta	Comments
	-----	-----	-----	-----	-----	-----	-----
1-1	-0.514	-152.0	-152.5	0.745			
1-2	-0.508	-153.0					
2-1	-0.508	-228.6	-228.1	0.745	-75.6		
2-2	-0.508	-227.6					
3-1	-0.508	-307.4	-306.6	1.209	-78.4		
3-2	-0.508	-305.7					
Substance	Calibr.	Y.reg/offset		Slope		Nonlin.	Mean deviat.
	-----	-----		-----		-----	-----
FuMa	std.add.	-1.521e-007		-3.697e-005			6.947e-010
Final results				+/- Res. dev.	%	Comments	
	-----			-----		-----	
FuMa =	4.937 mg/g			0.066	1.336		

Method for the determination of the sum of maleic and fumaric acid in malic acid with the 746 VA Trace Analyzer

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====						
Method: AB179 .mth OPERATION SEQUENCE						
Title : Determination of Fumaric and Maleinic acid						

	Instructions	t/s	Main parameters		Auxiliary parameters	
	-----	-----	-----		-----	
1	SMPL>M		V.fraction	mL	V.total	L
2	DOS>M		Soln.name	HCl	V.add	1.000 mL
3	PURGE					
4	STIR	300.0	Rot.speed	2000 /min		
5	(ADD					
6	PURGE					
7	STIR	30.0	Rot.speed	2000 /min		
8	ØSTIR					
9	ØPURGE	5.0				
10	(REP					
11	SEGMENT		Segm.name	polaro		
12	REP)1					
13	ADD>M		Soln.name	FuMa_Std	V.add	0.050 mL
14	ADD)2					
15	END					
Method: AB179 SEGMENT polaro						

	Instructions	t/s	Main parameters		Auxiliary parameters	
	-----	-----	-----		-----	
1	DME		U.ampl	-25 mV	t.meas	20.0 ms
2	DPMODE		t.step	0.60 s	t.pulse	40.0 ms
3	SWEEP	42.0	U.start	-300 mV	U.step	6 mV
			U.end	-700 mV	Sweep rate	10 mV/s
4	ØMEAS		U.standby	mV		
5	END					

Method 2

Separate determination of maleic and fumaric acid

Reagents

All used reagents must be of purest quality possible (p.a. or suprapur). Only high purity water is used to prepare the solutions.

- Hydrochloric acid, suprapur, w(HCl) = 30%
- Ammonia solution, suprapur, w(NH₃) = 25%
- Sodium hydroxide, suprapur, w(NaOH) = 30%
- Fumaric acid: puriss p.a., CAS 110-17-8
- Maleic acid: puriss p.a., CAS 110-16-7

Ready-to-use solutions

- Ammonium buffer pH 9.6: c(NH₄Cl) = 1 mol/L, c(NH₃) = 2 mol/L
Add to 112.5 mL ammonia and 53 mL hydrochloric acid enough distilled water to make 500 mL.
- Maleic acid standard solution: β(maleic acid) = 1 g/L
Dissolve 100 mg maleic acid in dist. water and add 2 mL ammonium buffer. Ad-

just the pH value to 8.0 with sodium hydroxide and fill up to 100 mL with dist. water.

- Fumaric acid standard solution: $\beta(\text{fumaric acid}) = 1 \text{ g/L}$
Dissolve 100 mg fumaric acid in dist. water and add 2 mL ammonium buffer.
Adjust the pH value to 8.0 with sodium hydroxide and fill up to 100 mL with dist. water.

Analysis

Measuring solution:

10 mL (diluted) sample
+ 1 mL ammonium buffer

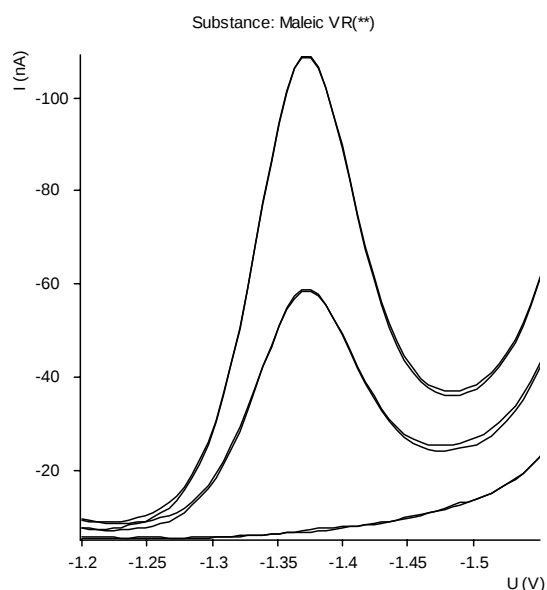
Adjust the pH value to 8 with sodium hydroxide or hydrochloric acid. The polarogram is recorded with following parameters:

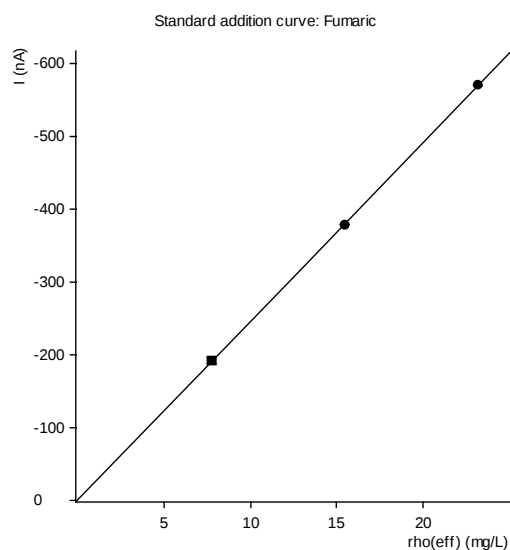
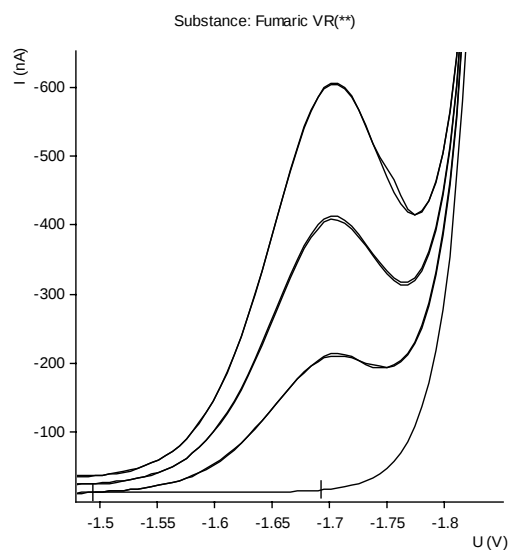
working electrode	DME
stirrer speed (rpm)	2000
mode	DP
purge time	300 s
equilibration time	5 s
pulse amplitude	50 mV
start potential	-1200 mV
end potential	-1900 mV
voltage step	6 mV
measure time	20 ms
pulse time	40 ms
voltage step time	0.6 s
sweep rate	10 mV/s
peak potential:	Maleic acid Fumaric acid
	-1380 mV -1700 mV

The concentration is determined by standard addition.

Example

Separate determination of maleic and fumaric acid in malic acid with the 746 VA Trace Analyzer
(1 g malic acid in 100 mL dist. water, 2 mL polarographed)





Sample volume 1 g

Results < LOD Maleic acid

5.0 mg/g Fumaric acid

Report

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===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====
Determ.      : 11241743      User: zu      Date: 1999-11-24
Modified     : no            Run : 2          Time: 17:43:06
Sample table: -
```

Pos.	Ident.1/S1	Ident.2/S2	Ident.3/S3	Method.call	Sample size/S0
	Malic Acid	1.0			1 g

```
Method : AB179_2
Title  : Separate determination of Fumaric and Maleic acid
Remark1: Determination of Fumaric and Maleic Acid in DL-Malic Acid
Remark2:
```

Substance	Maleic	Comments
Mass conc.:	-	Mass : -
MC.dev.:	-	Add.mass : 25 ug
Cal.dev.:	-	V0.sample: -

VR	U/mV	I/nA	I.mean	Std.dev.	I.delta	Comments
00	-					
01	-					
10	-1371	-41.52	-41.88	0.5172		
11	-1370	-42.25				
20	-1370	-85.29	-85.71	0.6015	-43.83	
21	-1370	-86.14				

Substance	Fumaric	Comments
Mass conc.:	50.45 mg/L	Mass : 100.9 ug
MC.dev.:	0.739 mg/L (1.46%)	Add.mass : 100 ug
Cal.dev.:	-	V0.sample: 2 mL

VR	U/mV	I/nA	I.mean	Std.dev.	I.delta	Comments
00	-1693	-189.3	-191.9	3.645		
01	-1698	-194.5				
10	-1696	-375.7	-376.0	0.3510	-184.1	
11	-1697	-376.2				
20	-1699	-561.3	-560.3	1.453	-184.3	
21	-1698	-559.3				

Substance	Techn.	Y.reg/offset	Slope	Nonlin.	Mean deviat.
Maleic	std.add.	5.942e-10	-2.275e-05		1.052e-09
Fumaric	std.add.	-1.913e-07	-2.464e-05		2.275e-09
Final results			+/- Res.dev.	%	Comments
Maleic =	0.0000 g/g		0.000	-	var. not found
Fumaric =	5.0447 mg/g		0.074	1.46	

Method for the separate determination of maleic and fumaric acid with the 746 VA Trace Analyzer

===== METROHM 746 VA TRACE ANALYZER (5.746.0101) =====						
Method: AB179_2 .mth			OPERATION SEQUENCE			
Title : Separate determination of Fumaric and Maleic acid						

	Instructions	t/s	Main parameters		Auxiliary parameters	
	-----	-----	-----		-----	
1	SMPL>M		V.fraction	2.000 mL	V.total	0.1 L
2	DOS/M		V.added	11.000 mL		
3	REM		10 mL H2O, 1 mL buffer			
4	PURGE					
5	STIR	300.0	Rot.speed	2000 /min		
6	(ADD					
7	(REP					
8	PURGE					
9	STIR	30.0	Rot.speed	2000 /min		
10	ØSTIR					
11	ØPURGE	5.0				
12	SEGMENT		Segm.name	polaro		
13	REP)1					
14	ADD>M		Soln.name	Ma_Std	V.add	0.025 mL
15	ADD>M		Soln.name	Fu_Std	V.add	0.100 mL
16	ADD)2					
17	END					
Method: AB179_2			SEGMENT polaro			

	Instructions	t/s	Main parameters		Auxiliary parameters	
	-----	-----	-----		-----	
1	DME					
2	DPMODE		U.ampl	-50 mV	t.meas	20.0 ms
			t.step	0.60 s	t.pulse	40.0 ms
3	SWEEP	72.0	U.start	-1200 mV	U.step	6 mV
			U.end	-1900 mV	Sweep rate	10 mV/s
4	ØMEAS		U.standby	mV		
5	END					