

Determination of Calcium and Magnesium with a Ca-ISE

Determination of Ca and Mg in aqueous solutions, mineral water, and milk by complexometric titration with EDTA using a Ca-ISE and a reference electrode.

Sample	Various different samples: Ca standard solutions, mineral water, milk drink.	Preparation and Procedures Method 34 1) Dissolve 2-20 g of the sample in deion. water. 2) Adjust the pH value to pH 12 with NaOH, 1.0 mol/L (autom.) 3) Titrate wit EDTA, 0.1 mol/L Method 22 4) Dissolve a second sample (same sample) in deion. water 5) Adjust the pH value to pH10 6) Titrate wit EDTA, 0.1 mol/L Method principle: 1) The calcium and magnesium content is determined with method 22. Both ions are complexed at pH10. 2) The calcium content is determined with method 34. Mg(OH) ₂ precipitates at pH12 and thus only calcium is complexed by EDTA.
Substance	Calcium, Ca, M(Ca) = 40.08 Magnesium, Mg, M(Mg) = 24.305	
Chemicals	Buffer NH ₃ /NH ₄ Cl NaOH, c(NaOH) = 1.00 mol/L	
Titrant	EDTA, c(EDTA) = 0.1 mol/L	
Standard	Ca standard, 1g/L	
Instruments	DL70ES / DL77 DL58 / DL55+ (with plus-dongle)	
Accessories	2 burette drives DV90 2 Burettes DV1010 Balance , PC with LabX Software, Titration beakers ME-101974	
Indication	DG111, DX240 Ca-ISE electrode DX200, outer bridge electrolyte 3M KCl	
Chemistry	1) Ca ²⁺ + EDTA = Ca-EDTA + 2H ⁺ at pH 10 and at pH 12. 2) Mg ²⁺ + EDTA = Mg-EDTA + 2H ⁺ at pH 10	
Calculation	Titration at pH 12: R1=Q[2]*C/m, C=M*1000/z, ppm Ca R2=Q[2], stored as aux. value H1 Titration at pH 10: R1=Q, mmol of Ca and Mg R2=(Q - H1)*C2/m C2= M*1000/z , ppm Mg	
Waste disposal	Very alkaline waste. Neutralize with an acid before final disposal.	
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		Remarks Provided the sample gives a smooth curve the termination criteria can be changed to stop after the first EQP Results of other samples 1) Standards Ca and Mg. Nominal content : Ca:1000mg/L, Mg: 100mg/L Results Mg Number results R1 n = 3 Mean value x = 97.21 ppm Mg Standard deviation s = 0.7332 Rel. standard deviation srel = 0.754 % Results Ca Number results R2 n = 3 Mean value x = 999.72 ppm Ca Standard deviation s = 2.359 Rel. standard deviation srel = 0.0.236 % 2) Milk drink. Nominal content: 900mg/100g Results Ca Number results R1 n = 3 Mean value x = 894.9 mg/100g Standard deviation s = 8.282 Rel. standard deviation srel = 0.926%

Results

34 Content Ca Date: 28-Oct-2002 12:46 pm
 28-Oct-2002 13:12 Titrator: DL58
 SW Version 2.4

Results

No.	ID	Sample Size	Results
1/1	Water	20.0 mL	407.92 ppm Ca 0.204 mmol
1/2	Water	20.0 mL	401.01 ppm Ca 0.200 mmol
1/3	Water	20.0 mL	401.44 ppm Ca 0.200 mmol

Statistics

Number results R1 n = 3
 Mean value x = 403.46 ppm Ca
 Standard deviation s = 3.8734
 Rel. standard deviation srel = 0.960 %

Statistics

Number results R2 n = 3
 Mean value x = 0.201
 Standard deviation s = 0.0019
 Rel. standard deviation srel = 0.960 %

22 Content Ca, Mg Date: 28-Oct-2002 14:37 pm
 28-Oct-2002 14:54 Titrator: DL58
 SW Version 2.4

Results

No.	ID	Sample Size	Results
1/1	Water	20.0 mL	0.24 mmol 0.204 ppm
1/2	Water	20.0 mL	0.24 mmol 0.200 ppm Mg
1/3	Water	20.0 mL	0.24 mmol 0.200 ppm Mg

Statistics

Number results R1 n = 3
 Mean value x = 0.24
 Standard deviation s = 0.00129
 Rel. standard deviation srel = 0.546 %

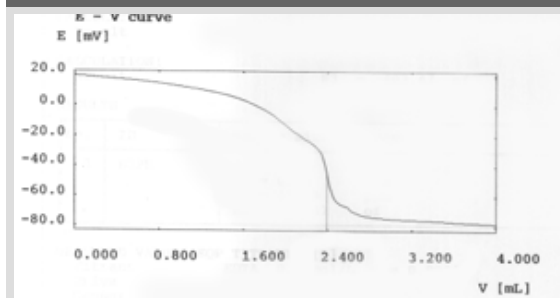
Statistics

Number results R2 n = 3
 Mean value x = 43.04 ppm Mg
 Standard deviation s = 1.571
 Rel. standard dev srel = 3.65

Table of measured values

	Volume mL	Increment mL	Signal mV	Change mV	1st deriv. mV/mL	Time min:s
	2.2370	0.0510	-24.5	-2.3	-44.3	2:07
	2.2810	0.0440	-26.8	-2.3	-51.4	2:12
	2.3150	0.0340	-29.2	-2.5	-72.2	2:18
	2.3360	0.0210	-31.1	-1.9	-92.3	2:23
	2.3560	0.0200	-34.3	-3.2	-158.3	2:29
	2.3760	0.0200	-39.0	-4.7	-235.9	2:38
	2.3960	0.0200	-46.8	-7.8	-387.7	2:48
	2.4160	0.0200	-53.0	-6.2	-310.2	2:59
	2.4360	0.0200	-57.4	-4.5	-222.9	3:07
	2.4560	0.0200	-60.8	-3.4	-168.0	3:13
	2.4760	0.0200	-63.0	-2.2	-109.9	3:19
	2.5140	0.0380	-65.3	-2.3	-61.2	3:24
	2.5900	0.0760	-67.5	-2.2	-28.9	3:30
	2.6110	0.0210	-69.1	-1.6	-73.9	3:35
	2.6310	0.0200	-70.2	-1.2	-58.2	3:41
	2.6780	0.0470	-71.3	-1.1	-23.4	3:46
	2.6990	0.0210	-72.2	-0.8	-40.0	3:52
	2.7340	0.0350	-72.8	-0.6	-18.5	3:57
	2.7660	0.0320	-73.5	-0.6	-20.2	4:02
	2.8300	0.0640	-74.1	-0.6	-9.1	4:08
	2.8930	0.0630	-74.6	-0.5	-8.2	4:13
	3.0190	0.1260	-75.2	-0.6	-4.6	4:19
	3.1690	0.1500	-75.7	-0.5	-3.4	4:25
	3.3190	0.1500	-76.2	-0.5	-3.4	4:30
	3.4690	0.1500	-76.6	-0.5	-3.0	4:36
	3.6190	0.1500	-77.1	-0.5	-3.0	4:42
	3.7690	0.1500	-77.5	-0.5	-3.0	4:48
	3.9190	0.1500	-77.9	-0.4	-2.6	4:53
	4.0000	0.0810	-78.3	-0.4	-4.8	4:59

Titration curve



Method

Method	34	Content Ca
Version	28-Oct-2002	13:14
Title		
Method ID	34	
Title	Content Ca	
Date/time	30-Jul-1999	13:14
Sample		
Sample ID	D3PH	
Entry type	Weight	
Lower limit [g]	2.0	
Upper limit [g]	25.0	
Molar mass M	40.08	
Equivalent number z	1	
Titration stand	Stand 1	
Temperature sensor	Manual	
Stir		
Speed [%]	60	
Time [s]	10	
EP titration		
Titrant/Sensor		
Titrant	NaOH	
Concentration [mol/L]	0.1	
Sensor	DG111	
Unit of meas	pH	
Predispensing		
Volume [mL]	to volume	
Volume [mL]	0.5	
Titrant addition		
Mode	Dynamic	
dE(set) [mV]	8.0	
dV(min) [mL]	0.02	
dV(max) [mL]	0.15	
dE [mV]	1.0	
dt [s]	1.0	
t(min) [s]	2.0	
t(max) [s]	10.0	
End point		
Potential	12	
Tendency	Positive	
Termination		
at maximum volume [mL]	10.0	
Delay [s]	10	
EQP titration		
Titrant/Sensor		
Titrant	EDTA	
Concentration [mol/L]	0.1	
Sensor	DX240	
Unit of meas	mV	
Predispensing		
Mode	No	
Titrant addition		
Mode	Dynamic	
dE(set) [mV]	2.0	
dV(min) [mL]	0.05	
dV(max) [mL]	0.1	
Measure mode		
Mode	Equilibrium controlled	
dE [mV]	1	
dt [s]	2.0	
t(min) [s]	3.0	
t(max) [s]	30.0	
Recognition		
Threshold	50.0	
Steepest jump only	Yes	
Range	No	
Tendency	Negative	
Termination		
at maximum volume [mL]	5.0	
at potential	Yes	
at slope	No	
afternumber EQPs	No	
comb. term. conditions	No	
Evaluation		
Procedure	Standard	
Potential 1	No	
Potential 2	No	
Stop for reevaluation	No	
Calculation		
Formula	$R=Q[2]*C/m$	
Constant	$C=M*1000/z$	
Decimal places	2	
Result unit	ppm	
Result name	Tot. Ca	
Statistics	Yes	
Calculation		
Formula	$R2=Q[2]$	
Constant		
Decimal places	3	
Result unit	mmol	
Result name	Consumption	
Statistics	Yes	
Auxiliary value		
Formula	$H1=x[2]$	
Report		
Output	Printer	
Results	No	
All results	Yes	
Raw results	Yes	
Table of measured values	Yes	
Sample data	Yes	
E - V curve	Yes	
dE/dV - V curve	Yes	

Method	22	Content Ca, Mg
Version	28-Oct-2002	14:37
Title		
Method ID	22	
Title	Content Ca, Mg	
Date/time	28-Oct-2002	14:37
Sample		
Sample ID	D3PH	
Entry type	Weight	
Lower limit [g]	0.0	
Upper limit [g]	25.0	
Molar mass M	24.305	
Equivalent number z	1	
Titration stand	Stand 1	
Temperature sensor	Manual	
Dispense		
Titrant	Ca buffer	
Concentration [mol/L]	0.1	
Volume [mL]	10	
Stir		
Speed [%]	50	
Time [s]	10	
EQP titration		
Titrant/Sensor		
Titrant	EDTA	
Concentration [mol/L]	0.1	
Sensor	DX2400	
Unit of meas	mV	
Predispensing		
Mode	No	
Titrant addition		
Mode	Dynamic	
dE(set) [mV]	2.0	
dV(min) [mL]	0.02	
dV(max) [mL]	0.15	
Measure mode		
Mode	Equilibrium controlled	
dE [mV]	1	
dt [s]	2.0	
t(min) [s]	5.0	
t(max) [s]	30.0	
Recognition		
Threshold	50.0	
Steepest jump only	Yes	
Range	No	
Tendency	Negative	
Termination		
at maximum volume [mL]	5.0	
at potential	No	
at slope	No	
afternumber EQPs	No	
comb. term. conditions	No	
Evaluation		
Procedure	Standard	
Potential 1	No	
Potential 2	No	
Stop for reevaluation	No	
Calculation		
Formula	$R=Q$	
Constant		
Decimal places	3	
Result unit	mmol	
Result name	Consum.	
Statistics	Yes	
Calculation		
Formula	$R=(Q-H1)*C2/m$	
Constant	$C=M*1000/z$	
Decimal places	2	
Result unit	ppm	
Result name	Content Mg	
Statistics	Yes	
Report		
Output	Computer+Printer	
Results	Yes	
All results	Yes	
Raw results	Yes	
Table of measured values	Yes	
Sample data	No	
E - V curve	Yes	
dE/dV - V curve	No	