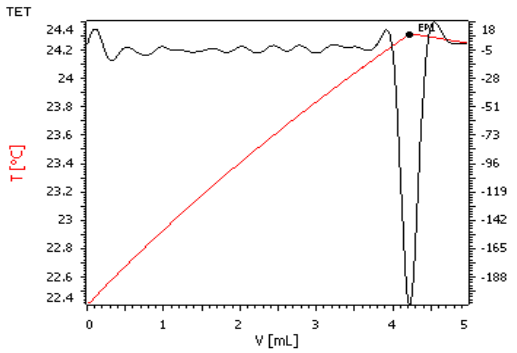
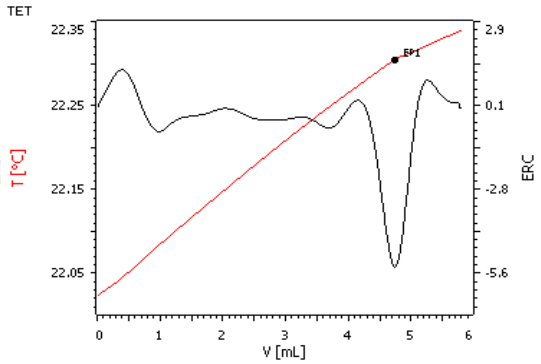
Titration Application Note H–126

Determination of silver and nitric acid in silver electrolyte bath



Plot of Ag with NaCl



Plot of HNO_3 with NaOH

Silber and nitric acid are determined in silver electrolyte solutions by using thermometric titration. The method provides accurate results in a short time and is ideally suited for routine process control.

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Method description

Principle

A customer has reportedly experienced difficulties with potentiometric titrimetric procedures and has submitted two acidic solutions of silver electrolyte to establish the feasibility of determining the silver and nitric acid contents by thermometric titration.
Nominal concentrations of 350 g/L Ag and 3 g/L HNO_3 were given as guidelines. Based on these parameters, it was decided to use 1 mol/L NaCl to determine the Ag content by thermometric precipitation titration and determine the HNO_3 content using 0.1 mol/L NaOH in a thermometric acid-base titration.

Samples

Silver electrolyte baths.

Sample preparation

Dilution of customer samples.

Configuration

Basic equipment list for automated titration

2.814.0030	814 USB Sample Processor
2.859.0010	859 Titrotherm
6.2041.340	Sample rack 24 × 75 mL
6.9011.020	Thermoprobe
6.1459.400	Sample beaker/75 mL
2.802.0010	Rod Stirrer
6.1909.020	Stirring propeller (104 mm)
2.800.0010	2 × 800 Dosino
6.3032.210	2 × Dosing Unit 10 mL
6.6056.222	*tiamo*™

Solutions

Titrant for Ag	1 mol/L NaCl, prepared from A.R. NaCl, (dried for 4 hours at 110 °C) and deionized water.
Titrant for HNO_3	0.1 mol/L NaOH, prepared by diluting standardized 2 mol/L NaOH solution

Analysis

Determination of Ag in electrolyte solution

Dilute 10 mL by bulb pipette to 250 mL with deionized water in a volumetric flask, and titrate 25 mL aliquots in 75 mL polypropylene titration vessels with 1 mol/L NaCl solution. The 25 aliquot is equivalent to 1 mL of original solution.

Determination of HNO_3 in electrolyte solution

A 5 mL aliquot of solution was diluted to 25 mL in a 75 mL polypropylene titration vessel, and directly titrated with 0.1 mol/L NaOH according to the following basic titration conditions. Based on previous experience, an average value was assumed for the titration blank.

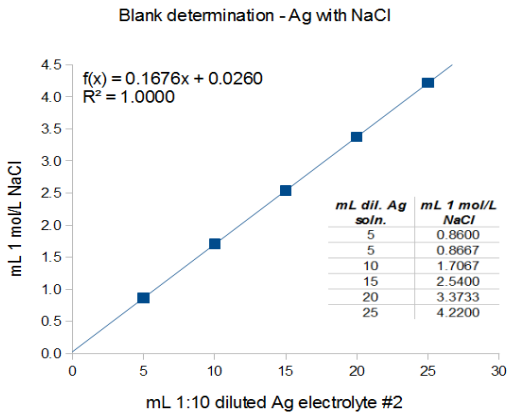
Titration blank for the Ag determination

For highly accurate work, it is necessary to determine the systematic error («blank») of the determination. This exercise is performed once only, during the initial set-up of the system.
A diluted solution is prepared according to 3.1. above. Aliquots of 5, 10, 15, 20 and 25 mL are pipetted into titration vessels, and made to ~25 mL with deionized water. The aliquots are titrated according to the conditions outlined in 3.1. above.

A regression analysis of the results is performed, where mL of diluted solution (x-axis) are plotted against mL of NaCl titrant consumed. The y-intercept value is the systematic error of the determination, and is subtracted from each endpoint volume. It is stored in *tiamo*™ software as a Common Variable («CV»).

Systematic error («blank») estimation for Ag determination

The regression curve for estimation of the systematic error is illustrated below:



The systematic error was estimated to be 0.0260 mL.

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Method description

Parameters

Main titration parameters for Ag determination

Titrant dose rate (mL/min)	4
ERC EP1 (exothermic)	–100
Data smoothing («filter factor»)	50
Stirring speed (802 Rod Stirrer)	15

Main titration parameters for HNO_3 determination

Titrant dose rate (mL/min)	6
ERC EP1 (exothermic)	–3
Data smoothing («filter factor»)	28
Stirring speed (802 Rod Stirrer)	15

Calculations

$g/L\ Ag^+ = ((EP1 - blank) \times C01 \times C02)/C00$
$g/L\ HNO_3 = ((EP1 - blank) \times C01 \times C02)/C00$

EP1 = endpoint in mL
C00 = sample weight in mL
C01 = concentration of titrant in mol/L
C02 = molecular weight of Ag^+ (107.8682 g/mol)
C02 = molecular weight of HNO_3 (63.01284 g/mol)

Results and discussion

Determination of Ag content

A summary of results is given in the following table:

Table 1. Ag determination – repeatability

Dil 10 mL>250mL>25 mL aliquot = 1 mL original solution

Sample #1		Sample #2	
mL 1mol/L NaCl	***Ag g/L***	***mL 1mol/L NaCl***	***Ag g/L***
3.5133	376.59	4.2267	453.62
3.5067	375.87	4.2200	452.90
3.5133	376.59	4.2133	452.18
3.5067	375.87	4.2200	452.90
3.5133	376.59	4.2200	452.90
3.5133	376.59		
average	**376.35**		**452.90**
std dev	**0.37**		**0.51**
% rsd	**0.10**		**0.11**

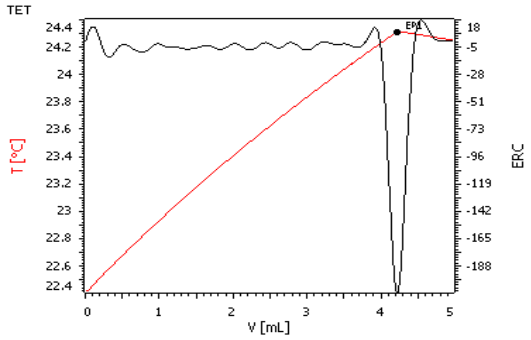
At a percentage relative standard deviation of approximately 0.1%, analytical precision is considered good. The actual time of titration is approximately one minute.

Determination of HNO_3 content

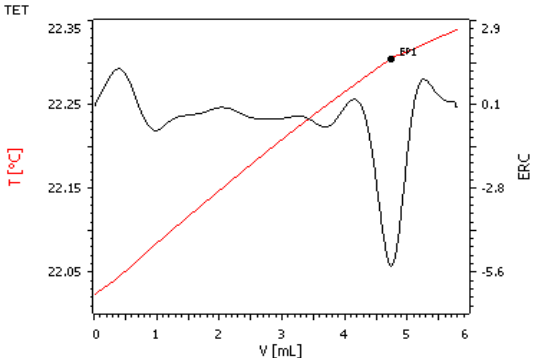
A summary of results is given in the following table:

Sample #1 = 5 mL aliquot		***Sample #2 = 5 mL aliquot***	
mL 0.1 M NaOH	**HNO_3 g/L**	**mL 0.1 M NaOH**	**HNO_3 g/L**
4.710	6.1	1.960	2.5
4.720	6.1	1.950	2.5
4.730	6.1	1.960	2.5
4.740	6.1	1.960	2.5
4.760	6.1	1.980	2.5
average	**6.1**		**2.5**
std dev	**0.02**		**0.01**

Titration plots



Plot of Ag with NaCl



Plot of HNO_3 with NaOH

Legend

Red curve = titration solution temperature, black curve = second derivative of temperature curve (used to

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Method description

accurately locate endpoint inflections in temperature curve)

Conclusion

Thermometric titration by Metrohm 859 Titrotherm provides rapid, precise, accurate, and trouble-free solutions for the determination of silver and nitric acid in silver electrolyte baths.

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