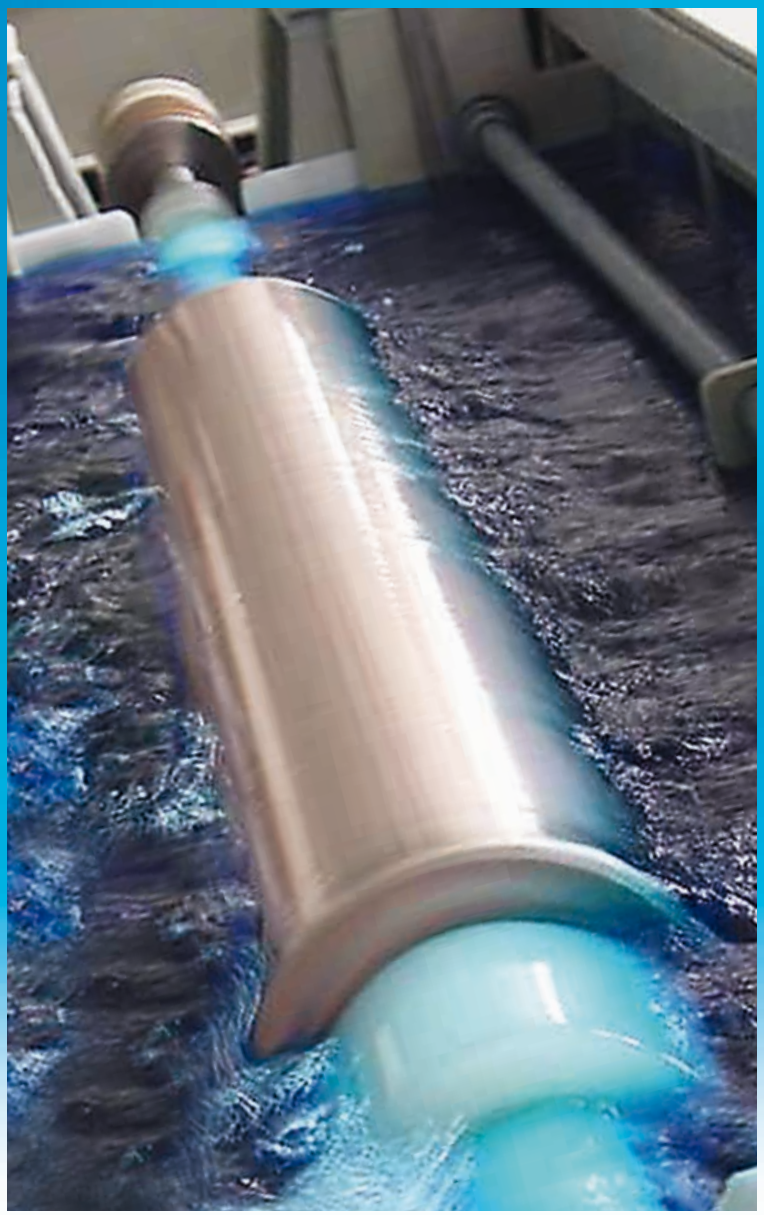
Electroplating Guide



Complete automation of titration methods

Electroplating Guide

Automated Sample Analysis

METTLER TOLEDO

Editorial

Dear Reader

Titration, when compared with most other analytical methods, accommodates an enormous variety of sample types. Accordingly, a variety of methods are commonly used to determine the contents of metal ions, acids, bases, and other electroplating bath components. Each and every method contains several steps and is adapted to only one bath component.

The need for efficiency and safety when running this variety of electroplating bath determination methods obviously demands automation. However, with such a wide variety of process steps and sample types effective automation the titration process from start to finish has proven elusive. Now, innovative sample changers and technologies give operators the ability to run titrations in an essentially automated manner from sample preparation to titration, results calculation, documentation, and even cleaning/conditioning of electrodes and accessories.

Operators must also have an easy ability to switch from routine to specific analysis depending on the day's work schedule, as well as the possibility to adapt equipment for future requirements or expansion.Of course, the ability to run such varied processes and to meet such needs requires instrument versatility, flexibility, modularity and reliability.

METTLER TOLEDO's titrators, autosamplers and accessories are designed to cope with such requirements and to assist with more than simply going from sample to sample. They can provide efficient analyses, eliminated transcription errors, and enable flexible, process-driven workflow automation.

This Electroplating Guide is fully dedicated to the automation of the entire titration method. Three sections cover the following topics:

- **Section 1:** A customer case study entitled "Automated Titration of Coating Baths," which describes the advantages of a fully automated titration system in context
- **Section 2:** Two selected electroplating titration applications focusing on electroless copper baths/copper determination and on the determination of nickel in an electroless nickel bath
- **Section 3:** Completely automated titration methods: Descriptions of enabling technologies, products and solutions applying METTLER TOLEDO InMotion™ Autosampler, SmartCodes™, SmartSample™ and the Liquid Handler. It shows how the appropriate use of these solutions helps manage titration automation with ease.

We hope you find this information useful as you seek to improve sample workflow, processing ease, and results accuracy in your own electroplating bath titrations

Mettler-Toledo

Content

1. Customer Case Study: Automated Titration of Coating

Analysis of electroplating baths is critical when specific quality requirements of plated materials must be achieved. For many electroplating bath composition parameters titration is the method of choice thanks to its versatility and general acceptance. Titration also accommodates for high concentrations of analytes where other techniques require extended dilutions prior to analysis.

The customer's case

Collini has produced hard chromium coatings for the machine industry since 1890 in Vienna. In the past twenty years, the company has become a specialist for "tribological coatings" for the automobile industry. The range of products includes coatings such as hard chromium, Triflon®, Glatox® and Skintech® as pure metal coatings, metal oxide coatings, or dispersion composite coatings. They fulfill a large number of the requirements of suppliers of components to the automobile industry for wear resistance, controlled friction target values, corrosion resistance and decorative appearance for safety systems, drive systems, fuel systems, or locking systems.

Coatings require a thickness of 2 to 50 µm and are deposited exclusively from aqueous systems (electrolytically). Solutions used in these processes require daily testing in an in-house quality control laboratory. Density, pH and conductivity are checked, and the main inorganic constituents are quantified by titration. Results are used immediately to make any necessary corrections to the baths.

At least seventy samples have to be processed daily. Up until now, they have been manually prepared and titrated. Ing. Günther Krimshandl, laboratory technician in the central analytical laboratory, wanted to automate nickel and hypophosphite determinations to eliminate manual processing steps, save time, and free up technicians for other value-added tasks. He also hoped that automation would provide quicker, more repeatable results.

Simply allow to complex and oxidize

The nickel determination is a simple equivalence point titration with EDTA after murexide indicator and ammonia have been added to the sample. Murexide forms a green complex with nickel at pH 10. The EDTA displaces the murexide and forms a more stable complex with nickel. At the equivalence point, only nickel ions complexed with EDTA and free murexide indicator are present. This is shown by the color change from green to purple. The DP5 Phototrode™ detects the sharp color change at a wavelength of 550 nm and the titrator determines the point of inflection of the curve.

$Ni^{2+} + Murexide^{-} \rightarrow Ni\text{-}Murexide^{+}$
$Ni\text{-}Murexide^{+} + EDTA^{4-} \rightarrow Ni\text{-}EDTA^{2-} + Murexide^{-}$

The titration of sodium hypophosphite is somewhat more involved. Hypophosphite can be oxidized in solution, which would allow direct titration. A relatively weak oxidizing agent would have to be used, however. Otherwise, additional bath constituents would also be oxidized.

Iodine solution is the best choice. However, oxidation of hypophosphite with iodine is, a relatively slow reaction, which is why iodine cannot be used for direct titration – the titration would take hours. This difficulty is overcome by performing a back titration: A defined excess of iodine is added to the sample previously acidified with sulfuric acid and the mixture is allowed to stand closed for at least 25 min at room temperature in darkness until the entire hypophosphite content has been oxidized:

$I_2 + H_2PO_2^{-} + H_2O \rightarrow 2\ I^{-} + HPO_3^{2-} + 3H^{+}$

The excess iodine can now be simply and quickly titrated back with sodium thiosulfate according to the following reaction equation:

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

The equivalence point is detected with the DM140-SC Redox electrode and the titrator automatically calculates the original hypophosphite content.

The content of orthophosphate is determined in a similar way. In contrast to the hypophosphite titration, however, sodium hydrogencarbonate is first added instead of sulfuric acid in order to make the solution alkaline for the oxidation.

Immediately before titration, the solution is acidified with acetic acid. The automated hypophosphite method is described in greater detail in the section that follows. Orthophosphate titration can be automated and performed in a similar way.

Steps performed in parallel with Titration Excellence

The three titrations required for these multi-step determinations can be automated nicely with the help of METTLER TOLEDO Excellence titrators. In Collini's case, a T90 titrator was connected to two Rondo 20 sample changers to simultaneously and independently perform the different analyses. The first Rondo is used to determine the nickel content of up to 20 samples, while the hypophosphite or orthophosphite content of the same samples is titrated on the second Rondo (Fig. 1).

Figure 1:
The Titration Excellence system titrates nickel and hypophosphite in parallel including sample preparation.

Special attention was paid to the automation of sample preparation steps. For example, in the nickel determination, the ammonia is added using an SP250 peristaltic pump and water for dilution added with a membrane pump. Similarly, in the hypophosphite titration, the sulfuric acid and the water are automatically dispensed into the titration beaker using SP250 pumps.

The iodine solution for back titration is very accurately dosed with a burette. Since each hypophosphite sample is first prepared and then allowed to stand for 25 min, other samples can be prepared in the meantime using two sample loops.

The first loop executes the preparation of all samples. Afterward, the first sample is sent to the Rondo titration tower and the second loop (titration) is started provided that at least 25 min have elapsed since the first sample was prepared (Fig. 2). Otherwise, the system waits for the remaining time to elapse before starting the back titration.

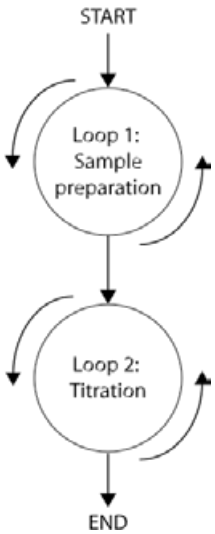


Figure 2: First, all samples run through Loop 1. After the last sample has been prepared, all samples run through Loop 2.

Flexibility of timing optimizes efficiency

Since the number of samples in a series can vary between 1 and 19, valuable time would be wasted if the sample waiting time between loops were always the same. Short series need less preparation time than long ones. Therefore, the waiting time with a short series must be longer than with a larger one.

This problem is solved through clever timing: An auxiliary value is defined before the first loop and set to zero. After each sample, this auxiliary value is defined as the sum of its previous value plus tUSE, where tUSE is the time that has elapsed since the start of the particular sample. When all samples have run through the first loop, the auxiliary value has increased to exactly the time that has elapsed since the preparation of the first sample. Now the second loop begins in the method process, at the beginning of which there are four special stirrer functions.

The first function stirs for 20 min, the second for 15 min, the third for 10 min and the fourth for 5 min. The stirrer speed is set to 0% — in other words, it does not actually stir; it merely introduces a waiting time. Only the stirrer functions needed to allow the first sample to wait for at least 25 min are processed so that the iodine can completely react with the hypophosphite.

To select the right stirrer function, each of the four functions includes a condition that takes the value of the auxiliary value determined in the first loop into account. If this value is less than 10 min, it "stirs" for 20 min. If it is between 10 and 15 min, it "stirs" for 15 min, and so on. If the auxiliary value is already greater than 25 min, no stirring occurs and the titration is immediately begun (Fig. 3).

In this way, sufficient time is always allowed for the reaction to occur irrespective of the number of samples being processed. Hence, no time is wasted.

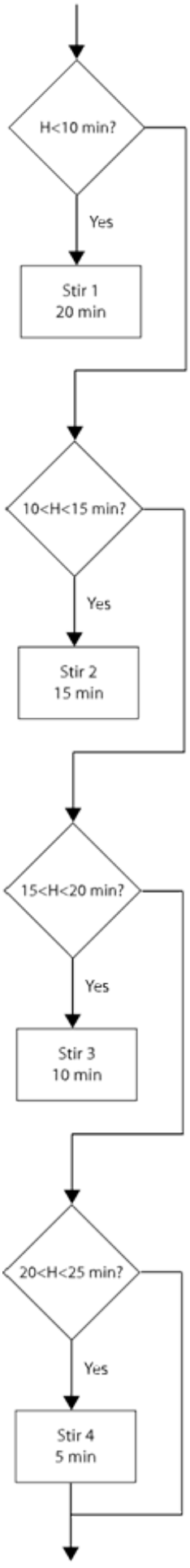


Figure 3: Depending on how long the first loop takes to prepare all the samples, the first sample is not titrated until the first sample has been allowed to react for at least 25 min.

Reaction in the dark thanks to CoverUp™

Iodine reactions with hypo- and orthophosphite must be performed in complete darkness. For this reason, red titration beakers are used that do not transmit light of wavelengths that interfere with the reaction. The samples are also equipped with a lid that blocks light transmission and prevents the escape of iodine, which would affect results. The lid also suppresses nearly all of the unpleasant smell of ammonia vapor.

Adding the reliable CoverUp™ lid handling device allows removal of the lid from the titration beaker immediately before titration and replacing it again afterward (Fig. 4). CoverUp also helps reduce unpleasant odor and ensure that the reaction completes without outside disturbances while further enabling the automated nature of the process.

Sample data is entered at the PC and the analyses are started. LabX titration PC software controls the Titration Excellence system and stores results data for easy retrieval and evaluation.

Figure 4: CoverUp™ removes the lid immediately before titration and closes the titration beaker again immediately afterwards. This prevents unpleasant vapors from escaping.

Rapid and reliable results

The titration time for the daily load of at least 70 samples has been significantly reduced. Automated sample preparation and analysis workflows have reduced the entire process from 10 man hours to 4.5 titrator hours. Because results are known earlier, reaction to changes of the bath composition is faster.

Results are now more reliable than before when up to three different people performed the analyses.

Collini is very pleased with the advantages of the system and with the support provided by METTLER TOLEDO for applications and service.

Günther Krimshandl is very satisfied: "The system has fulfilled our requirements regarding the degree of automation and exceeded our expectations regarding stability. The time from taking the sample to the availability of the measurement value has significantly decreased, while at the same time the reproducibility of the measurement values has improved."

Figure 5: Titrator Excellence with new InMotion sample changer

2. Selected Titration Applications for the Electroplating Industry

This section provides an overview of two common electroplating bath titrations using selected Mettler-Toledo instruments and equipment to automate the determinations.

2.1. Electroless copper bath: Determination of copper (Application M 062)
2.2. Electroless nickel bath: Determination of nickel (Application M 066)

Note: Since these applications were established, some products have been replaced.

Former product	**Current product**
Sample changer Rondo 20	InMotion (several models available e.g. InMotion Flex 100 mL)
Software LabX pro titration	LabX 2014
Analytical balance XP205	XPE205

For more details: Titration Application Brochure 4.1, METTLER TOLEDO, ME 724561A (2013)

METTLER TOLEDO **Application M062**

Electroless Copper Bath: Determination of Copper

Method for determination of copper in electroless copper bath by iodometric titration.

Sample	Electroless copper bath,10 mL (see "Preparation")
Compound	Copper (Cu^{2+}), M = 63.54 g/mol, z = 1, Copper Sulfate ($CuSO_4$), M= 159.60 g/mol, z = 1, Copper Sulfate Pentahydrate ($CuSO_4.5H_2O$), M = 249.68 g/mol, z = 1
Chemicals	25% Sulfuric acid, 40 mL 10% Potassium iodide, KI, 5 mL 10% Potassium thiocyanate, KSCN, 5 mL.
Titrant	Sodium thiosulfate, $Na_2S_2O_3$ c($Na_2S_2O_3$) = 0.1 mol/L
Standard	Potassium iodate, KIO_3 20-30 mg
Indication	DMi140-SC (Combined platinum ring redox electrode)
Chemistry	$2CuSO_4 + 4KI + \rightarrow 2CuI + 2K_2SO_4 + I_2$ $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$
Calculation	R_1 = Q*C/m, g/L (Cu content) R_2 = Q*C/m, g/L ($CuSO_4$) R_2 = Q*C/m, g/L ($CuSO_4.5H_2O$) C = M/z Q = Titrant consumption in mmol. m = mass of the sample in mL M = Molar mass of sample in g. z = Equivalent number of sample
Waste disposal	Copper solutions : If necessary, neutralize the solution before final disposal as special waste
Author, Version	Ruby Das, IMSG AnaChem, Version 2.0, Revised: C. De Caro, MSG AnaChem

Preparation and Procedures

CAUTION

- Use safety goggles, a lab coat, wear mask and gloves. Always work in a fume hood.
- Ensure cleaning of sensor after each titration.

Sample Preparation: Electroless copper bath

- Take 158 mL deionized water in 200 mL volumetric flask add 2 mL Cu-bath Ginplate Cu 406-C with stirring.
- While stirring add 20mL Ginplate Cu 406-B and 20 mL Ginplate Cu 406-A.

(Literature: GINPLATE CU 406)

Sample titration:

- Dispense 10 mL of sample from additional dosing unit to the titration beaker placed on sample changer.
- Add 40 mL of 25% H_2SO_4 from peristaltic pump.
- Add 5 mL of 10% KI from additional dosing unit.
- Add 5 mL of 10% KSCN from additional dosing unit.
- Wait for 5 minutes with stirring
- Titrate with 0.1mol/L $Na_2S_2O_3$.
- After completion of each sample, sensor, stirrer and titration tubes are rinsed by deionized water by means of membrane pump.
- Sensor is cleaned with deionized water in conditioning beaker placed on sample changer after each sample.

Remarks

- The method parameters have been optimized for the sample of this application. It may be necessary to adapt the method to your specific sample.
- This method allows a fully automated analysis procedure. This method can be easily modified for manual operation. Select "Manual stand" in the method function "Titration stand"
- Purity of potassium iodate used is 99.5%.

Literature:

- Ginplate Cu 406, (www.growel.com/tds/796.pdf), a trademark of Grauer & Weil India Ltd, www.growel.com
- Mettler-Toledo Applications M062 and M009.

Instruments	- Titration Excellence T70/T90 (Other Titrators: depending on instrument type, manual operation and method changes are necessary) - Rondo 20 Sample Changer with PowerShower™ (MT-51108003) - XP 205 Balance
Accessories	- 3 x Additional dosing unit (MT-51109030) - 3 x 10 mL DV1010 glass burette (MT-51107501) - 1 x 5 mL DV1005 glass burette (MT-51107500) - 100 mL Polypropylene titration beakers (MT-00101974) - Peristaltic pump SP250 (MT-51108016) - LabX® pro titration software

Results

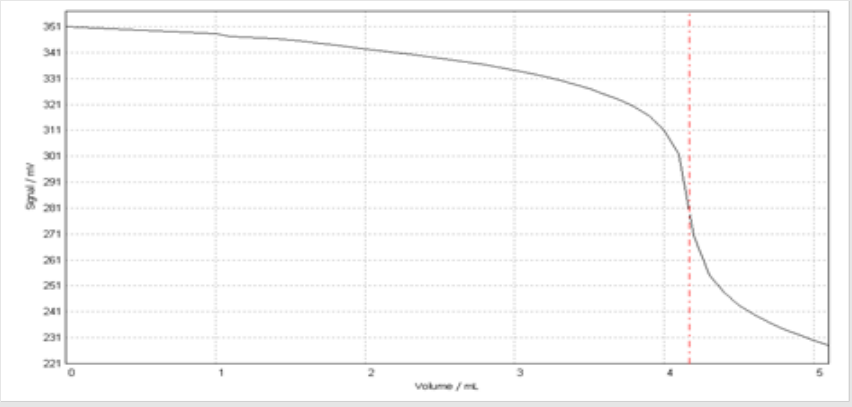
Results

Method-ID	Copper		
Sample	10 mL		(1/6)
Cu	2.663	g/L	
$CuSO_4$	6.688	g/L	
$CuSO_4.5H_2O$	10.463	g/L	
Sample	10 mL		(2/6)
Cu	2.663	g/L	
$CuSO_4$	6.689	g/L	
$CuSO_4.5H_2O$	10.464	g/L	
Sample	10 mL		(3/6)
Cu	2.668	g/L	
$CuSO_4$	6.701	g/L	
$CuSO_4.5H_2$	10.483	g/L	
Sample	10 mL		(4/6)
Cu	2.668	g/L	
$CuSO_4$	6.702	g/L	
$CuSO_4.5H_2O$	10.485	g/L	
Sample	10 mL		(5/6)
Cu	2.663	g/L	
$CuSO_4$	6.688	g/L	
$CuSO_4.5H_2O$	10.463	g/L	
Sample	10 mL		(6/6)
Cu	2.664	g/L	
$CuSO_4$	6.692	g/L	
$CuSO_4.5H_2O$	10.469	g/L	

Statistics

Method-ID	Copper	
R1	Copper	
Samples	6	
Mean	2.665	g/L
s	0.002	g/L
srel	0.093	%
R2	$CuSO_4$	
Samples	6	
Mean	6.693	g/L
s	0.007	g/L
srel	0.097	%
R3	$CuSO_4.5H_2O$	
Samples	6	
Mean	10.471	g/L
s	0.010	g/L
srel	0.097	%

Titration curve



	Volume mL	Increment mL	Signal mV	Change mV	1st deriv. mV/mL	Time s	Temperature °C
	0.0000	NaN	351.1	NaN	NaN	0	25.0
	1.0000	0.1000	348.3	-2.8	NaN	4	25.0
	1.1000	0.1000	347.3	-1.0	NaN	7	25.0
	1.2000	0.1000	347.0	-0.3	NaN	10	25.0
	1.3000	0.1000	346.6	-0.4	NaN	13	25.0
	1.4000	0.1000	346.3	-0.3	-4.94	16	25.0
	1.5000	0.1000	345.8	-0.5	-4.69	19	25.0
	1.6000	0.1000	345.3	-0.5	-6.07	22	25.0
	1.7000	0.1000	344.6	-0.7	-6.78	25	25.0
	1.8000	0.1000	343.9	-0.7	-7.19	28	25.0
	1.9000	0.1000	343.1	-0.8	-7.18	31	25.0
	2.0000	0.1000	342.4	-0.7	-7.00	34	25.0
	2.1000	0.1000	341.8	-0.6	-6.79	37	25.0
	2.2000	0.1000	341.1	-0.7	-6.78	40	25.0
	2.3000	0.1000	340.4	-0.7	-7.02	43	25.0
	---	---	---	---	---	---	---
	3.8000	0.1000	320.0	-2.8	-33.46	89	25.0
	3.9000	0.1000	316.5	-3.5	-76.65	92	25.0
	4.0000	0.1000	311.1	-5.4	-122.03	96	25.0
	4.1000	0.1000	301.5	-9.6	-153.00	104	25.0
EQP1	4.169456	NaN	279.8	NaN	-159.19	NaN	NaN
	4.2000	0.1000	270.3	-31.2	-158.95	122	25.0
	4.3000	0.1000	255.3	-15.2	-138.10	130	25.0
	4.4000	0.1000	248.4	-6.9	-97.40	134	25.0
	4.5000	0.1000	243.5	-4.9	-52.08	139	25.0
	4.6000	0.1000	240.1	-3.4	-21.68	142	25.0
	4.7000	0.1000	237.1	-3.0	NaN	145	25.0
	4.8000	0.1000	234.4	-2.7	NaN	148	25.0
	4.9000	0.1000	232.0	-2.4	NaN	151	25.0
	5.0000	0.1000	230.0	-2.0	NaN	154	25.0
	5.1000	0.1000	228.1	-1.9	NaN	157	25.0

Comments

- **Be careful!** If cyanide is present in the sample the addition of a sulfuric acid solution must be performed in a ventilated fume hood (formation of poisonous HCN!).
- This electroless copper bath is used for chemical copper deposition on printed circuit boards. It consists of sodium hydroxide, formaldehyde, weakly complexed copper, free complexing agent(s), and additives.
- Titer determination of 0.1 mol/L $Na_2S_2O_3$ is done as per the Mettler-Toledo application M009 and mean value found is 1.00509. The mean value of the titer is automatically stored as part of the setup by the function TITER.

Principle :

- A weaker copper complex is decomposed at room temperature by the acid medium. A stronger complex is decomposed in the same way at elevated temperature.
- After decomposition the sample is cooled at room temperature.
- Then potassium iodide (KI) and potassium thiocyanate (KSCN) are added.
- Cu(II) is reduced with excess iodide (I^-) and subsequently precipitated as CuI in the presence of thiocyanate (SCN^-). KSCN is added to avoid adsorption of I_2 on the surface of CuI :

  $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

- The amount of iodine formed is proportional to the Cu (II) content. Cover the beakers to avoid loss of iodine. The complete reduction of Cu (II) requires 5 min.
- The liberated I_2 is then titrated at room temperature with $Na_2S_2O_3$.

  $2 S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

- Stir moderately. Vigorous stirring causes loss of I_2.
- Alternative: Photometric indication with DP5 Phototrode™ ; indicator : starch

001 Title

Type	General titration
Compatible with	T70/T90
ID	Copper
Title	Determination of copper
Author	admin
.....	

002 Sample

Number of IDs	1
ID 1	Copper
Entry type	Fixed volume
Volume	10.0 mL
Density	1.0 g/mL
Correction factor	1.0
Temperature	25.0°C

003 Titration stand (Rondo/TowerA)

Type	Rondo/TowerA
Titration stand	Rondo60/1A
Lid handling	No

004 Dispense (normal) [1]

Titrant	CU SAMPLE
Concentration	1
Volume	10.0 mL
Dosing rate	60.0 mL/min
Condition	No

005 Pump

Auxiliary reagent	H2SO4 25%
Volume	40.0 mL
Condition	No

006 Dispense (normal) [2]

Titrant	10% KI
Concentration	1
Volume	5.0 mL
Dosing rate	60.0 mL/min
Condition	No

007 Dispense (normal) [3]

Titrant	10% KSCN
Concentration	0.1
Volume	5.0 mL
Dosing rate	60.0 mL/min
Condition	No

008 Stir

Speed	40 %
Duration	10 s
Condition	No

009 Instruction

Instruction	1
Mode	Time interval
Time interval	300 s
Print	Yes
LabX command	No
Condition	No

010 Titration (EQP) [1]

Titrant	
Titrant	Na2S2O3
Concentration	0.1 mol/L
Sensor	
Type	mV
Sensor	DM140-SC
Unit	mV
Temperature acquisition	
Temperature acquisition	No
Stir	
Speed	40 %
Predispense	
Mode	Volume
Volume	1.0 mL
Wait time	0
Control	
Control	User
Titrant addition	Incremental
dV	0.1 mL
Mode	Equilibrium controlled
dE	0.5 mV
dt	1.0 s
t (min)	3.0 s
t (max)	30.0 s
Evaluation and recognition	
Procedure	Standard
Threshold	100.0 mV/mL
Tendency	Negative
Ranges	0
Add. EQP criteria	No
Termination	
At Vmax	10.0mL
At potential	No
At slope	No
After number of recognized EQPs	Yes
Number of EQPs	1
Combined termination criteria	No
Accompanying stating	
Accompanying stating	No
Condition	
Condition	No

011 Calculation R1

Result	Cu
Result unit	g/L
Formula	R1=Q*C/m
Constant	C=M/z
M	M[Copper]
z	z[Copper]
Decimal places	3
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Condition	No

012 Calculation R2

Result	CuSO4
Result unit	g/L
Formula	R2=Q*C/m
Constant	C=M/z
M	M[Copper sulphate]
z	z[Copper sulphate]
Decimal places	3
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Condition	No

013 Calculation R3

Result	CuSO4.5H2O
Result unit	g/L
Formula	R3=Q*C/m
Constant	C=M/z
M	M[Copper sulphate pentahydrate]
z	z[Copper sulphate pentahydrate]
Decimal places	3
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Condition	No

014 Rinse

Auxiliary reagent	WATER
Rinse cycles	1
Vol.per cycle	10.0 mL
Position	Current position
Drain	No
Condition	No

015 Conditioning

Type	Fix
Interval	1
Position	Conditioning beaker
Time	10s
Speed	30%
Condition	No

016 End of sample

METTLER TOLEDO **Application M066**

Electroless Nickel Bath: Determination of Nickel

Method for determination of nickel content in electroless nickel bath.

Sample	Electroless nickel bath, 5 mL
Compound	Nickel, Ni M= 58.69 g/mol, z = 1
Chemicals	Deionized water, 50 mL Indicator : 0.2 g Murexide trituration with NaCl (1 : 500). Buffer pH10, 10 mL
Titrant	Ethylenediaminetetraacetic acid disodium, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ c(EDTA- Na_2) = 0.1 mol/L
Standard	Zinc Sulfate, $ZnSO_4$ c($ZnSO_4$) = 0.1 mol/L
Indication	DP5 Phototrode™ (555 nm) (Yellow to blue-violet)
Chemistry	Ni^{2+} + Murexide$^-$ → Ni-Murexide$^+$ Ni-Murexide$^+$ + $EDTA^{4-}$ → Ni-$EDTA^{2-}$ + Murexide$^-$
Calculation	R = Q*C/m*d, g/L Q = Titrant consumption in mmol. C = M/z. M = Molar mass of sample in g. z = Equivalent no. sample, z=1 d = density of sample in g/mL. m = mass of sample in mL.
Waste disposal	Nickel solutions : If necessary, neutralize the solution before final disposal as special waste.
Author, Version	Ruby Das, IMSG AnaChem, V2.0 Revised: C. De Caro, MSGAnaChem

Preparation and Procedures

CAUTION

- Use safety goggles, a lab coat and wear gloves. If possible, work in a fume hood.
- Ensure accurate cleaning of sensor is sufficient after each titration.

Sample Preparation:

- **Electroless nickel bath** : Pipette 20 mL Ginplate Ni 426-A and 20 mL Ginplate Ni 426-B in 200 mL volumetric flask and dilute it upto the mark with deionized water.

Sample titration:

- Add 0.25 g murexide trituration with NaCl (1:500) in the beaker placed on sample changer.
- Dispense 5 mL sample from dosing unit.
- Add 50 mL of deionized water from dosing unit.
- Add 10 mL of buffer pH10 from dosing unit.
- Titrate with 0.1mol/L EDTA.
- After completion of each sample sensor, stirrer and titration tubes are rinsed by deionized water by means of membrane pump.
- Sensor is cleaned with deion. water in the conditioning beaker placed on sample changer after each sample.

Remarks

- Prior to use , adjust the output signal of the DP5 Phototrode™ to approx. 1000 mV in deion.water before starting titration (100% transmission) by turning the small knob on the housing.
- Rinsing and conditioning of the Phototrode is crucial to achieve accurate and precise results.
- Avoid formation of bubbles during titration by low speed rate of stirrer, as they disturb photometric indication.
- This method allows a fully automated analysis procedure. This method can be easily modified for manual operation. Select “Manual stand” in the method function “Titration stand”.
- Sample may be added manually using a pipette instead of using an additional dosing unit.

Literature :

- Ginplate NI 426, (http://www.growel.com/tds/549.pdf), a trademark of Grauer & Weil India Ltd, www.growel.com
- Mettler-Toledo Application M066 and M007

Instruments	- Titration Excellence T50/T70/T90 (Other Titrators: depending on instrument type, manual operation and method changes are necessary) - XP205 Balance (MT-1106024) - Rondo 20 with PowerShower™ (MT-51108003)
Accessories	- 3 x Additional dosing unit (MT-51109030) - 1 x 20 mL DV1020 glass burette (MT-51107502) - 2 x 10 mL DV1010 glass burette (MT-51107501) - 1 x 5 mL DV 1005 glass burette (MT-51107500) - 100 mL Propylene titration beakers (MT-00101974)

Results

All results

Method-ID		Nickel determination
Sample		5 mL (1/6)
	R1 (Nickel)	5.44 g/L
Sample		5 mL (2/6)
	R2 (Nickel)	5.44 g/L
Sample		5 mL (3/6)
	R3 (Nickel)	5.45 g/L
Sample		5 mL (4/6)
	R4 (Nickel)	5.43 g/L
Sample		5 mL (5/6)
	R5 (Nickel)	5.43 g/L
Sample		5 mL (6/6)
	R6 (Nickel)	5.44 g/L

Statistics

Method-ID		Nickel determination
R1		Nickel
	Samples	6
	Mean	5.44
	s	0.01
	srel	0.138%

Titration curve

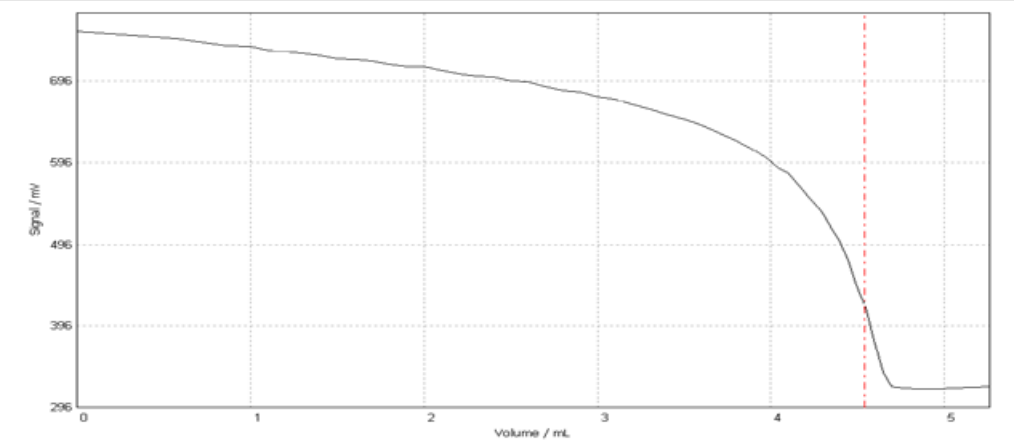


Table of measured values

	Volume mL	Increment mL	Signal mV	Change mV	1st deriv. mV/mL	Time s	Temperature °C
	0.000	NaN	757.2	NaN	NaN	0	25.0
	0.5715	0.5715	748.2	-9.0	NaN	5	25.0
	0.8570	0.2855	739.0	-9.2	NaN	13	25.0
	1.0000	0.1430	738.4	-0.6	NaN	16	25.0
	1.1000	0.1000	734.0	-4.4	NaN	20	25.0
	1.2000	0.1000	732.1	-1.9	-25.96	24	25.0
	1.3000	0.1000	729.6	-2.5	-24.64	28	25.0
	1.4000	0.1000	727.1	-2.5	-26.16	32	25.0
	1.5000	0.1000	723.3	-3.8	-24.72	37	25.0
	1.6000	0.1000	721.7	-1.6	-24.40	42	25.0
	1.7000	0.1000	720.6	-1.1	-23.28	44	25.0
	1.8000	0.1000	716.7	-3.9	-24.36	50	25.0
	1.9000	0.1000	713.5	-3.2	-28.28	55	25.0
	2.0000	0.1000	713.0	-0.5	-29.78	58	25.0
	2.1000	0.1000	708.5	-4.5	-30.43	62	25.0
	---	---	---	---	---	---	---
	4.3440	0.0500	518.0	-17.4	-358.17	184	25.0
	4.3940	0.0500	499.4	-18.6	-421.44	190	25.0
	4.4440	0.0500	476.6	-22.8	-538.07	196	25.0
	4.4940	0.0500	446.3	-30.3	-658.13	202	25.0
EQP1	4.540268	NaN	420.7	NaN	-659.56	NaN	NaN
	4.5440	0.0500	418.6	-27.7	-657.52	210	25.0
	4.5940	0.0500	379.1	-39.5	-544.67	218	25.0
	4.6440	0.0500	339.4	-39.7	-393.50	230	25.0
	4.6940	0.0500	322.0	-17.4	-269.40	239	25.0
	4.7600	0.6600	320.1	-1.9	-148.20	243	25.0
	4.8600	0.1000	319.3	-0.8	NaN	245	25.0
	4.9600	0.1000	319.6	0.3	NaN	248	25.0
	5.0600	0.1000	320.4	0.8	NaN	250	25.0
	5.1600	0.1000	321.2	0.8	NaN	253	25.0
	5.2600	0.1000	321.9	0.7	NaN	255	25.0

Comments

- Titer determination of 0.1 mol/L EDTA-Na_2 is done as per the Mettler –Toledo method applicatio M007 and mean value found is 0.99163.
- The mean value of the titer is automatically stored as part of the setup by the function TITER.
- The buffer pH 10 is prepared by dissolving 64 g NH_4Cl in 600mL 25% Ammonia solution and diluting upto the mark with deionized water in a 1L volumetric flask..
- The shape of the titration curve is somewhat affected by the concentration of the indicator. The results however do not differ significantly (tested range: 25-500 mg of Murexide trituration with NaCl(1 :500).
- Add the indicator before starting analysis. Keep sample free of air bubbles during titration. Air bubble and undissolved impurities affect the photometric indication.
- Due to the steep signal change, an EQP titration with fixed increments is used. The low threshol value allows for different amounts of indicator.

Principle :

- Nickel ions forms yellow complex with murexide in alkaline solution:

$$Ni^{2+} + Murexide^{-} \rightarrow Ni\text{-}Murexide^{+}$$

- By adding EDTA , Ni forms a more stable complex with EDTA:

$$Ni\text{-}Murexide^{+} + EDTA^{4-} \rightarrow Ni\text{-}EDTA^{2-} + Murexide^{-}$$

At the equivalence point, all Ni ions have been complexed by EDTA and murexide is free in the alkalin solution. There is a colour change from yellow to blue-violet.

Method

001 Title

Type	General titration
Compatible with	T50 / T70 / T90
ID	Nickeldetermination
Title	Ni determination
. . .	

002 Sample

Number of IDs	1
ID 1	Nickel
Entry type	Fixed volume
Volume	5.0 mL
Density	1.03 g/mL
Correction factor	1.0
Temperature	25.0°C
Entry	Arbitrary

003 Titration stand (Rondo/TowerA)

Type	Rondo/TowerA
Titration stand	Rondo60/1A
Lid handling	No

004 Dispense (normal) [1]

Titrant	NI SAMPLE
Concentration	1
Volume	5.0 mL
Dosing rate	60.0 mL/min
Condition	No

005 Dispense (normal) [2]

Titrant	Water..
Concentration	1
Volume	50.0 mL
Dosing rate	60.0 mL/min
Condition	No

006 Dispense (normal) [3]

Titrant	BUFFER 10PH
Concentration	1
Volume	10.0 mL
Dosing rate	60.0 mL/min
Condition	No

007 Stir

Speed	10%
Duration	60 s
Condition	No

008 Titration (EQP) [1]

Titrant

Titrant	EDTA(0.1M)
Concentration	0.1 mol/L

Sensor

Type	Phototrode
Sensor	DP5
Unit	mV

Temperature acquisition

Temperature measurement	No

Stir

Speed	10%

Predispense

Mode	Volume
Volume	1.0
Wait time	0 s

Control

Control	User
Titrant addition	Dynamic
dE (set value)	10 mV
dV (min)	0.05 mL
dV (max)	0.1 mL
Mode	Equilibrium controlled
dE	1.0 mV
dt	2 s
t (min)	2 s
t (max)	12 s

Evaluation and recognition

Procedure	Standard
Threshold	200.0 mV/mL
Tendency	None
Ranges	0
Add. EQP criteria	No

Termination

At Vmax	10.0 mL
At potential	No
At slope	No
Number of EQPs	1
Combined termination criteria	No

Accompanying stating

Accompanying stating	No

Condition

Condition	No

009 Calculation R1

Result	Ni content
Result unit	g/L
Formula	R1= Q*C/m*d
Constant	C=M/z
M	M[Nickel]
z	z[Nickel]
Decimal places	2
Result limits	No
Record statistics	Yes
Extra statistical func.	No
Send to buffer	No
Condition	No

010 Rinse

Auxillary reagent	WATER
Rinse cycles	1
Vol.per cycle	10 mL
Position	Current position
Drain	No
Condition	No

011 Condition

Type	Fix
Interval	1
Position	Conditioning beaker
Time	20 s
Speed	10 %
Condition	No

012 End of sample

3. Automation

Automation can help labs process more samples in less time, which can be very desirable in a competitive global manufacturing environment. As noted, however, effective automation of a titration process is often much more than just switching out samples.

A full range of autosamplers and accessories helps to fully automate the whole titration procedure from sampling, identification and temperature control to actual measurements and data gathering.

Based on process needs and degree of automation desired, Mettler-Toledo offers the following products that support different levels of automation:
- InMotion™ Autosampler – automated sample transport, dissolving and rinsing
- SmartSample™ – automatic identification and transfer of sample data
- SmartCode™ – automatic method detection
- Liquid Handler – automated liquid handling

A brief description of each enabling technology and its benefits follows.

3.1. InMotion™ Autosampler – Flexible, efficient autosampling

Quality control analyses are a must in many industry segments such as galvanic, chemistry, beverages or pharma. Samples are also tested using so-called at-line measurement directly in the plant rather than sending samples to a lab and waiting for results to arrive. In each case, however, automatic sample changers can contribute significant efficiency and safety to sample testing.

Whether QC or at-line, typically more than one parameter must be analyzed taking samples from different production sites. Each parameter requires a dedicated titration method and beyond that a different sample size due to the different analyte contents and regulation requirements. Thus, one has to perform several different sample preparation steps, several analyses execution tasks as well as several result calculation and documentation procedures.

Modern sample changers such as the InMotion™ Autosampler for titrators can automate many of these steps executing them repeatedly without fail. With such a system in place, the operator simply collects the samples from the different production sites, places them on an autosampler, and starts the respective method.

Innovation and modularity
The InMotion™ Autosampler transports the samples to the titration stand. InMotion also adds auxiliary reagents such as buffers or indicators, reactants, deionized water and solvents. It stirs the sample for a predefined time to dissolve it and mix it with other reactants if required. Such steps are carried out according to method specifications and free QC staff to complete other tasks.

However, QC staff may still frequently check the sampler visually to make sure all is okay. InMotion offers a much appreciated solution making these checks easier as well: One quick glance at the LED indicator light on the top of the titration tower lets operators know immediately if an analysis is still running, needs attention or is ready to run more samples.

Because large amounts of sample data must be transferred and managed when using autosamplers, InMotion also reads barcodes and SmartSample tags (see chapter 3.2) for easy, fast and secure data transfer.
Another feature example adding efficiency and safety to tirtation tasks is CoverUp™. Covering lids of the sample beakers are automatically lifted before the titration and put back immediately afterwards.

More advantages of InMotion include its reduced footprint which makes the most of bench space — a resource that is often quite limited in labs and QC stations, making installation of an automated titration system difficult. Accessories such as pumps or even a second titration tower can also be added neatly thanks to the sample changer's modularity while still maintaining the equipment's footprint.

Modularity of InMotion adds another advantage: The automated system can be tailored to the actual needs. Small or big sample racks, various sizes of sample beakers or a second titration tower bring just the right solution to run tests of the different baths in a very efficient and optimized way. The system can also easily be extended and adapted to future needs.

After completing a titration, a modern autosampler/ titration system also helps wash and rinse stands, beakers, stirrers, electrodes and other equipment parts freeing operators for more relevant tasks. METTLER TOLEDO's PowerShower™ option cleans the InMotion set-up thoroughly. The titration stand is washed during a multi-angle rinse sequence to ensure no carry over distorts the following sample. All wash phases occur automatically without user intervention.

Back titrations or titrations with several steps can also be performed and evaluated via fully automated procedures. InMotion and Titration Excellence instruments offer a comprehensive selection of opportunities.

Figure 6: InMotion sample changer details: Moving arm and titration head with and electrode.

3.2. SmartSample™ – Secure sample data transfer

Ensuring results are unquestionably allocated to the right sample can be difficult, particularly when a large number of various samples are being managed manually.

Keeping a sample's weight, size and ID together without doubt is just one task. Avoiding transcription errors when putting sample weights is another task. Remembering safely which sample is in which titration beaker is the third one.

Quantum of solace
Modern automatic titrators and sample changers provide good solutions to such problems of results allocation and misspelling. Above all, the SmartSample workflow support, a recent innovation by METTLER TOLEDO, improves sample preparation and delivers secure sample handling and sample data transfer.

No more beaker numbering, no more writing sample weights on beakers, papers or lab journals, no more confusing samples.

How does SmartSample work?

The RFID option of the new XPE and XSE Excellence balances sends (writes) sample ID and sample weight to the RFID tag of the titration beaker when weighing is complete. InMotion then reads all sample data once the beaker passes InMotion's RFID option and passes this information to the Excellence titrator.

The RFID tag of the sample beaker contains all sample data info such as ID and weight. Because the RFID tag is attached to a single beaker, the beakers can be placed in any sequence on the InMotion sample changer, with results still correlating safely to appropriate sample data.

Using SmartSample

Equip your XPE or XSE Excellence analytical balance and the InMotion sample changer with the respective RFID options (Figure 7, position 3 and 4). Then use titration beakers with RFID tags (Figure 7, position 2).
To automatically read sample ID barcodes, a barcode reader is linked to the balance (Figure 7, position 1).

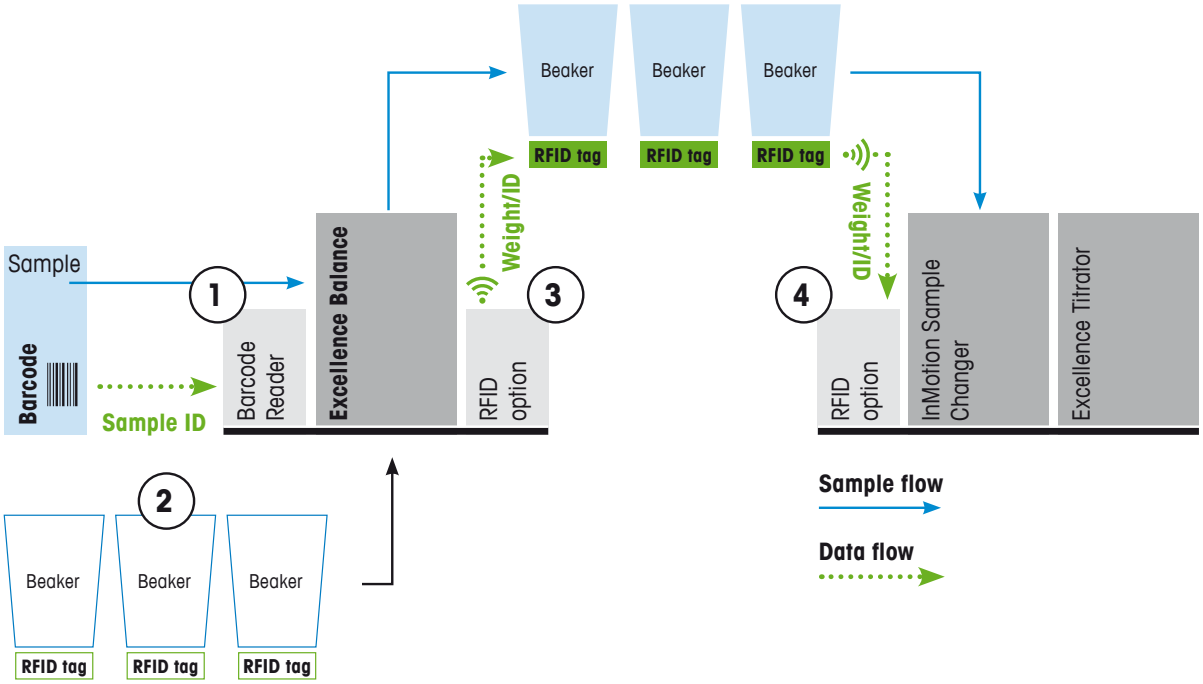


Figure 7: Secure sample weighing and data workflow with SmartSample

With the optimized SmartSample workflow, all sample information is entered once and at one place, while weighing in the samples at the analytical balance. The sample ID can be entered via barcode reader or manually using the balance terminal.

SmartSample then transfers sample weight and sample ID securely and efficiently to the titration instrument for subsequent analysis, eliminating sample mix-ups.

Figure 8: METTLER TOLEDO sample beaker with RFID smart tag

3.3. SmartCodes™ - Automated method assignment

When a QC lab or an at-line measurement station analyzes different samples, a dedicated method is applied for each sample to make sure samples are analyzed properly. For example, nickel determination is one method, hypophosphite is another, and orthophosphite a third.

Up to this point, the correct titration method needed to be selected at the titration instrument for each and every single sample or sample series. The method selection was entered manually observing the sample sequence. Thus, running samples in mixed order had to be avoided by all means.

A new way to assign methods
With a new feature of the LabX 2014 Titration PC software called SmartCode™, the method is automatically assigned to the sample. Based on sample ID, the LabX 2014 software automatically chooses the correct method and lets the titrator execute it.

The required sample ID can be barcoded on the beakers or stored on a RFID tag (see SmartSample above). InMotion autosamplers with respective accessories can read both barcoded and RFID tagged sample IDs on their own.

Figure 9: The SmartCode principle

Assigning the correct method to a particular sample automatically avoids worries, eliminates wasted samples and can save time by reducing rework.

Innovative combination
Let InMotion sample changer, SmartSample, SmartCode in combination with Excellence titrators and LabX 2014 work for you. Load an entire rack with all different samples requesting different methods and start the analyses with just one click.
Checking the status light of InMotion is the only duty left for you to know when the next sample load is due.

3.4. Liquid Handler – Versatile automated dosing

The Liquid Handler automated dosing system also opens new horizons in titration automation. It easily copes with a critical part of titration analytics crucial to obtain reliable results: The accurate and precise sampling of a representative aliquot of sample solution.

The Liquid Handler is fully integrated into the method concept of Excellence titrators. Dedicated method functions enable straightforward and comprehensive Liquid Handler programming to execute tasks such as aspirating sample, rinsing tubes or dosing solvent. Thus, it provides unsurpassed flexibility in automated dosing and pipetting of samples.

Two application examples are briefly explained below:
- Dosing of variable sample volumes
- Automation for continuous monitoring

3.4.1. Application example: Dosing of variable sample volumes

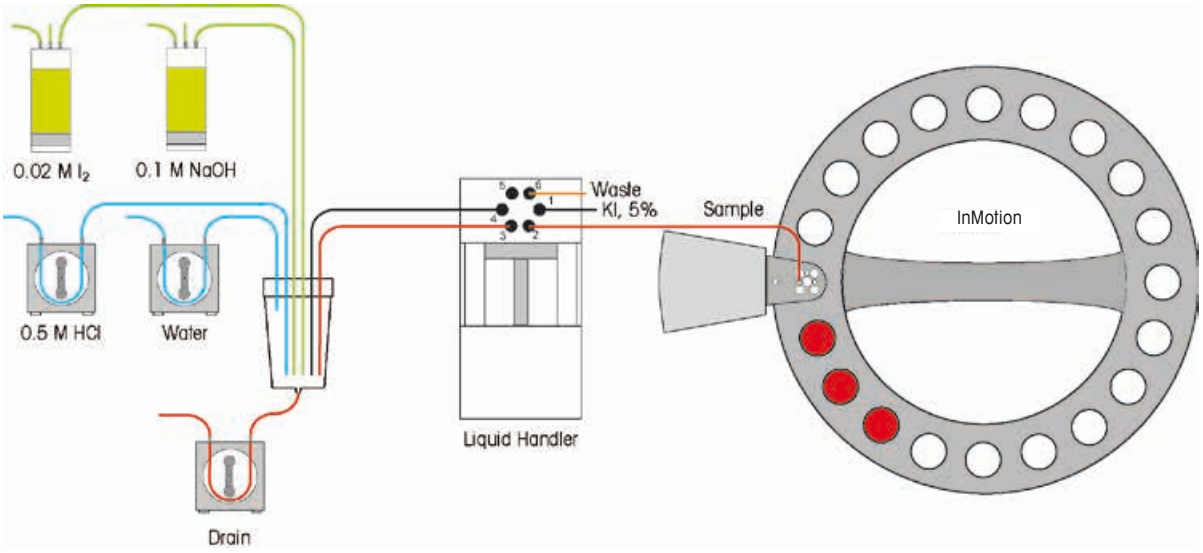
This automation example shows the dosing of variable volumes of sample. The example is taken from the automated analysis of red-wine vinegar. It includes the determination of the acetic acid and the SO2 content. Different sample sizes are required for each titration, 1 mL for the acid titration, 50 mL for the SO2 determination.

The acetic acid determination is a direct acid/base titration. Sodium hydroxide is the titrant, and a pH electrode is used as the sensor.
HOAc + NaOH → NaOAc + H2O

The sulfur dioxide is oxidized by iodine in acidic environment. Just before titration, some mL of 5% aqueous potassium iodide solution and 10 mL of diluted hydrochloric acid are added. The titrant used is iodine solution. For the voltametric indication a double pin platinum sensor is applied.

$SO_2 + I_2 + 2\ H_2O \rightarrow H_2SO_4 + 2\ HI$

The following drawing illustrates the setup:



Description of the automation process
The following steps are involved in the automation process:

1. Preparation of the Liquid Handler, i.e. thorough rinsing of the aspiration and dosing tubes in order to avoid any carry-over or contamination
2. First sampling cycle: Dosing of suitable sample volume (1 mL) and acid titration
3. Draining and cleaning of the equipment
4. Second sampling cycle: Dosing of suitable sample volume (50 mL), addition of acid and 5% KI solution and SO2 titration
5. Draining and cleaning of the equipment

For more details: Titration Application Brochure 40, Automatic Pipetting and Dosing.
METTLER TOLEDO, ME 51725111 (2009)

3.4.2. Application Example: Automation for continuous monitoring

This automation process may be applied for continuous monitoring of one or more parameters such as acidity or calcium content of process water, analysis of plating solutions (Ni, hypophospite), and salt content of effluents. Sampling and analysis may be directly performed at the production site.

Filtering of particulate matter
Frequently, analytes contain particles which require appropriate measures in order to prevent damage or blockage of the Liquid Handler multiport valve or burette glass cylinder. Filtering of the sample may be an option. However, a filter requires maintenance to avoid blockage. This maintenance can be automated, but it still requires manual inspection to ensure flawless unattended operation. The latter is counterproductive when fully automated, unattended operation is desired.

Superior procedure
A robust and excellent alternative to the filtering is sampling via peristaltic pump and subsequent pipetting of the suspension with the Liquid Handler . In general, the mechanical layout of peristaltic pumps is per se robust and suitable for the transfer of solid-containing liquid samples. The pump transfers an excess of sample into a beaker, where an aliquot is aspirated into a pipette tube connected to the Liquid Handler. Then, the residual sample is drained, the beaker rinsed, and the sample aliquot in the pipette tube flushed into the titration beaker with a defined amount of auxiliary reagent (e.g. water) provided by the Liquid Handler. Subsequently, the titration is performed and the titration beaker is then drained and rinsed again for the next sampling process.

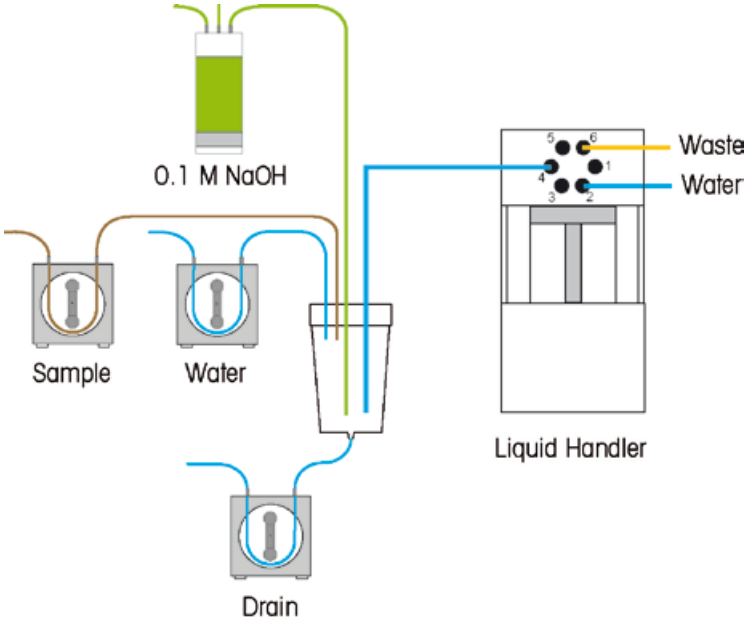
This sampling procedure is superior to filtering because of robustness and its reduced maintenance effort. Furthermore, the pipetting step excludes contamination and blockage of sensitive parts of the Liquid Handler. It ensures accurate dosing over the whole lifetime of the Liquid Handler, and the unit's usable operational time is greatly enhanced.

Acidity monitoring of process water
The determination of acidity is based on the well-known chemical neutralization reaction where HX stands for hydrochloric, sulfuric, nitric or other acids:

$$HX + NaOH \rightarrow NaX + H_2O$$

Each time 2 mL sample volume shall be used for the titration.

Illustration of the system setup:



Description of the automation process
The following steps are involved in automating this example process:

1. Preparation of the Liquid Handler, i.e. thorough rinsing of the pipetting tube
2. Preparation of the sample transfer line: rinsing with fresh sample
3. Draining and rinsing of the equipment
4. Transfer of fresh sample into titration beaker
5. Aspiration of defined sample volume into pipette tube
6. Draining and rinsing of equipment
7. Transfer of sample from pipette tube into titration beaker with defined amount of water provided by the Liquid Handler
8. Acid/base titration
9. Draining and rinsing of equipment

Start of the titration
The sampling process and subsequent titration may be launched in three different ways:

- Automatically using an external remote control system via RS232-C or TTL-input sent by this remote system. This requires a method structure including an auxiliary instrument method function waiting for a specific RS232 string.
- On operator's demand via shortcut on the touch screen display of the titrator – One Click® operation; or
- On demand via LabX titration software.

For more details: Titration Application Brochure 40, Automatic Pipetting and Dosing.
METTLER TOLEDO, ME 51725111 (2009)

4. Conclusion

As the composition of electroplating baths is crucial for the quality of the plated products, stringent bath analysis is a must. Titration provides for many parameters the method of choice. However, several analysis steps usually need to be executed which adds to the workload of supervisors and lab personnel.

Up-to-date titration instruments and in particular modern sample changers provide vast automation opportunities and eliminate at the same time sample handling hassles and workload pressure. Solutions like SmartSample, SmartCode and accessories such as LabX software and Liquid Handler help to fully automate titration methods from sample dosing to final result calculation and documentation.

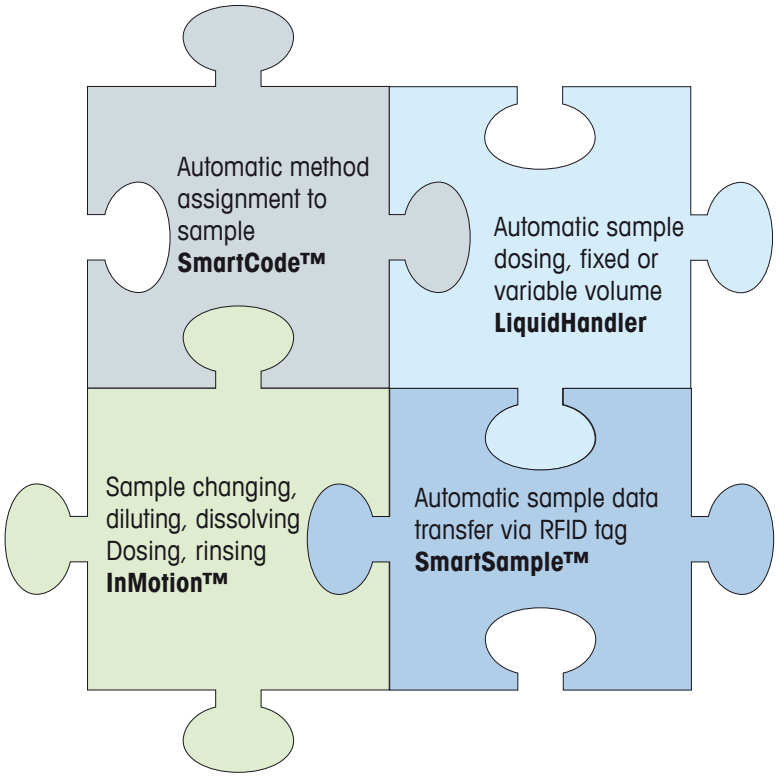


Figure 10: METTLER TOLEDO's solutions for automation can be combined and added to a comprehensive titration system.

Using these solutions together allows loading of an entire sample rack and starting the analyses with one click. Then, the automated titration system with Titration Excellence, InMotion sample changers and the respective accessories do the rest for you, freeing operators for other value-added tasks, increasing efficiency, reducing costs, and enhancing productivity.

5. Literature

1. Liquid Handling, Application Brochure 40. METTLER TOLEDO, ME 51725111 (2009)
2. Electronics and Electroplating Applications, Application Brochure 28. METTLER TOLEDO, (2007)
3. Selected Methods for Titration Excellence, Application Brochure 34. METTLER TOLEDO, ME 51725066 (2006)

Access Information and Know-how
on www.mt.com

The application chemists of the METTLER TOLEDO Analytical Chemistry market support group have prepared more than 500 of ready-made titration applications for use with the wide range of METTLER TOLEDO titrators. These proven and well-tested applications will help you to get accurate results quickly. Our online search engine allows you to search through the database.

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Risk-based guidelines for weighing, titration and pipetting from METTLER TOLEDO empower you to make the right decision when it really matters.

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GTP® reduces the risks associated with titration and facilitates
- compliance with regulations
- preservation of the accuracy and precision of results
- increased productivity and reduced costs
- professional qualification and training

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