nucomat

AUTOMATED ANALYSIS OF COPPER CONCENTRATES

INTRODUCTION

The need for analysing copper concentrates to determine the copper content accurately and rapidly is increasing.

Hence, there exists a demand for automated systems that perform the wet chemistry methods for the analysis of copper concentration in powder samples. Automation brings the advantage of increased hands-off capacity and improving accuracy and precision for routine analysis. It may even come with a considerable reduction in process cost.

Automation also provides an effective solution to the **tedious** process of sample preparation that expose laboratory staff to major **safety risks** when working with concentrated aggressive chemicals like boiling acids, strong bases and exposure to hydrofluoric acid vapours.

Manual sample prep procedure for Cu analysis.

AUTOMATED COPPER CONCENTRATE ANALYSIS

Nucomat has engineered an **automated platform for determining the typically between 10% to 50% copper in concentrated samples**. The platform provides industrial scale analytical capacity to process samples.
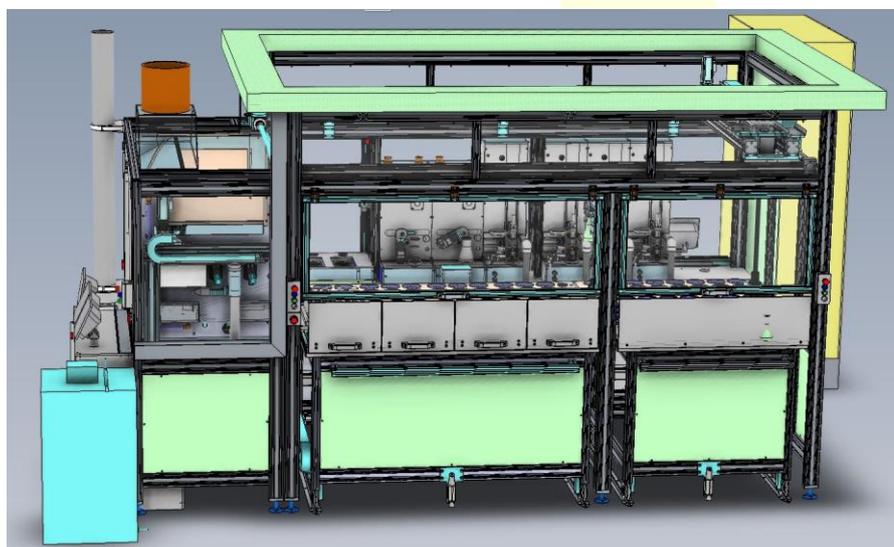
Technical design of the Copper concentrate system.

Starting with **gravimetrically dispensing** replicate powder samples at pre-set weights (between 100 and 1000 mg), followed by automated **Hotcell acid dissolution** and leaching steps and finally performs **Iodometric titration** using the colour change of starch as readout, similar to the manual process. Calibration of the titrant is performed with pure copper reference material.

Cu concentrate, Nucomat, 2020

MATERIALS AND METHODS

Sample dissolution is performed with hot acids. For samples containing between 20% and 30% copper about 400mg of the dry powder are dispensed in replicates into titration flasks and the sample weight recorded. A mixture of HNO_3 (68%), HCl (32%) and $HClO_4$ (70%) is dispensed in 10/5/3 volume ratio into the titration flask and heated to leach for up to 12 minutes on the Hotcell.
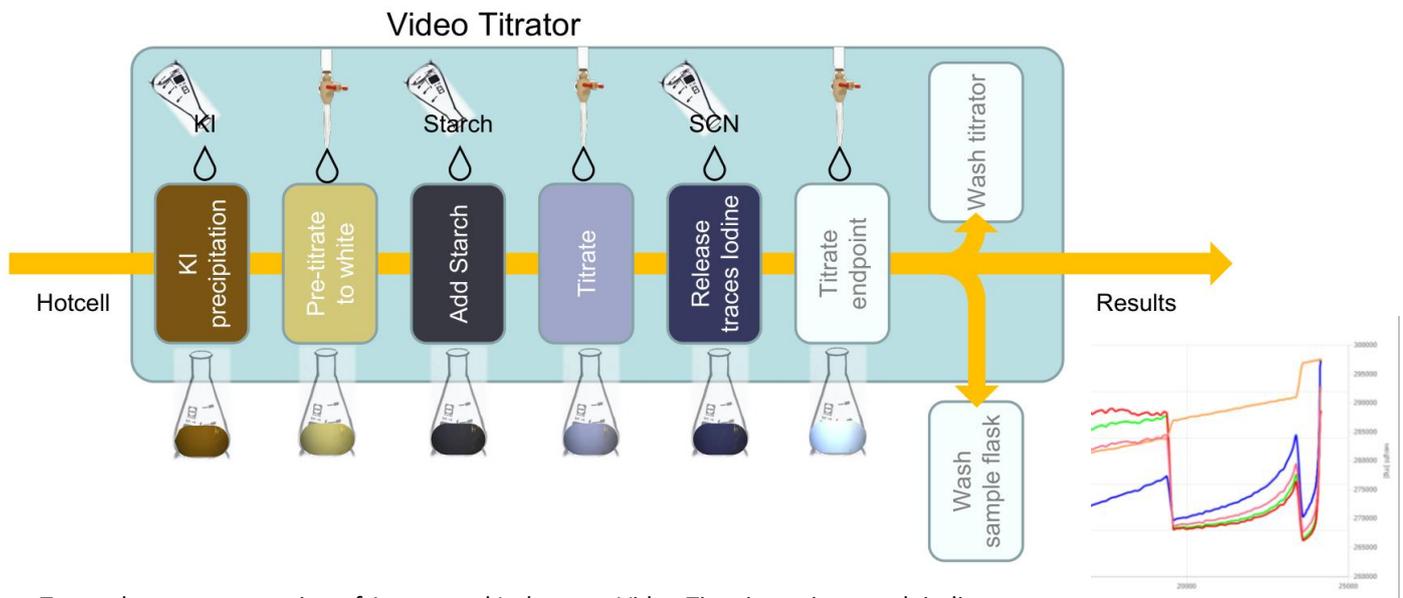
Pure copper is used as reference sample. 100 mg of reference sample is dispensed and dissolved in HNO_3 (68%) on the Hotcell, without addition of HCl or $HClO_4$. Excess liquid is evaporated from all samples for up to 20 minutes until an almost dry syrupy state is left at the bottom of the flask. After a cooling period the salts are dissolved in 25 mL water, re-heated for 5 minutes and allowed to cool down again on a swirl station.
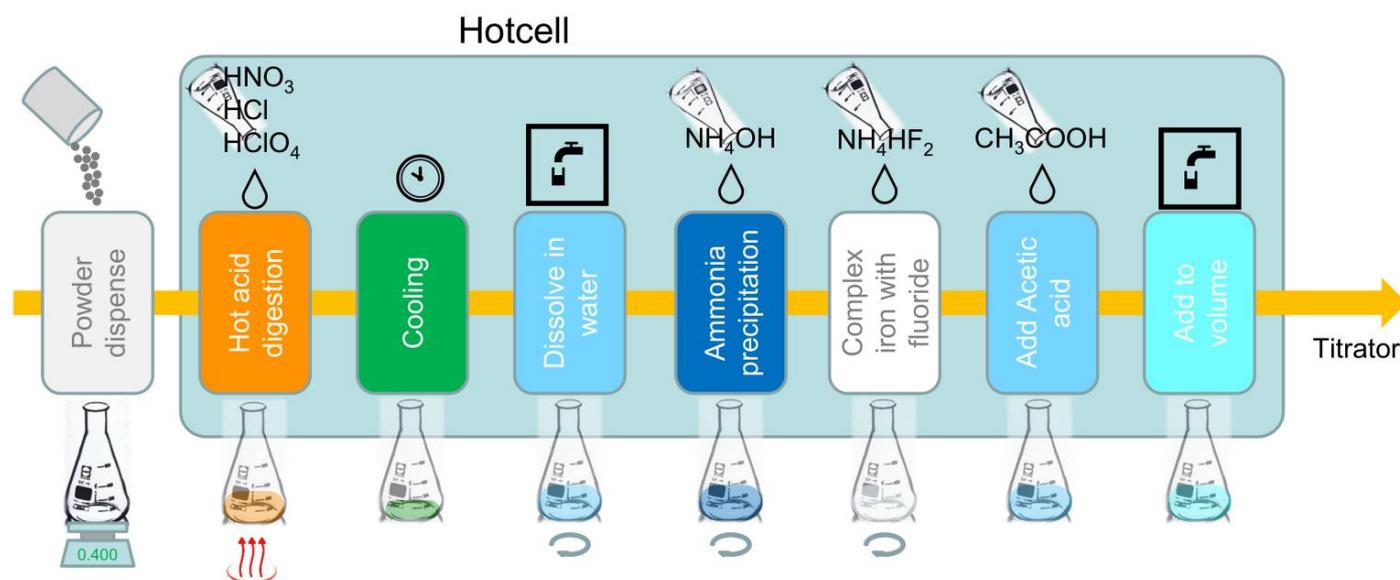
Automated sample preparation process with acid digestion in the Hotcell.

To neutralise the excess of acid 5 mL ammonia (25%) is added. Both iron and copper hydroxide are precipitated. The iron that will interfere with the titration is complexed with 20 mL NH_4HF_2 as a 20% (w/v) solution that is prepared fresh daily. Water is added to dilute the sample to about 100 mL and the sample acidified by adding 5 mL of glacial acetic acid.

The **iodometric titration** is based on oxidation of iodides to iodine by copper (II) ions, which get reduced to Cu^+ upon addition of excess KI. ($2Cu^{2+} + 4I^- \rightarrow 2CuI(s) + I_2$). 30 mL of a 10% (w/v) KI solution (made fresh daily) is added to the titration flask while mixing. The solution turns into a yellow-brown suspension. Thiosulfate titrant addition will convert free I_2 back to I^-, diminishing the blue colour from the starch – I_2 indicator complex. ($2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$). Titrant solution is made fresh daily with 19.618 g/L $Na_2S_2O_3.5H_2O$ and 25 mg/L NaOH. The titration is performed in 3 subsequent time series under video monitoring. First titrant is added until discolouration of the KI suspension. To the white suspension 2 mL of a 1% fresh starch solution is added. Secondly the titration is continued until the violet-blue colour is almost gone. Just before the equivalence point 5 mL of NH_4SCN 10% (w/v) is added to release the last traces of I_2 present, turning the solution again intense violet blue. Finally, titrant is added slowly until the equivalence point is reached with transition to a white solution as detected by the video titrator. The process is optimised in real-time by monitoring the colour changes and adjusting titration speed throughout the titration process: Fast in approach, slow and accurate near equivalence.

Video Titrator

Hotcell → KI precipitation → Pre-titrate to white → Add Starch → Titrate → Release traces Iodine → Titrate endpoint → Wash titrator / Wash sample flask → Results

KI | Starch | SCN

True colour representation of Automated Iodometry Video Titration using starch indicator.
Insert: Titration graph with subsequently: addition of starch, addition of SCN and equivalence point.
The yellow trace plots the gravimetric control values of the sample throughout the titration process.

All data from standards, sample replicates, individual reagent additions, and endpoint calculations are logged in the database with the sample replicate ID. Automated cleaning routines enable re-use of titration flasks on the system and prepare the titrator for running new samples without carry-over, and fully hands-off.

The standard automation setup with a capacity of up to 250 titrations daily, comprises:

- **2 powder samplers**: Automatically dispense and accurately weigh samples into titration flasks with gravimetric control.
- **16 position Hotcell:** A robotized fume hood for safe acid sample dissolution and leaching at high temperature.
- **2 acid and reagent dispensers:** prepare the reaction steps inside the Hotcell, accurately adding liquids like acids, bases and reagents with gravimetric control.
- **1 swirling position:** mix samples following addition steps and cool samples in the Hotcell.
- **2 wash stations** to automatically clean, rinse and re-use titration flasks after analysis.
- **4 video imaging titrators:** Proprietary titration stations to run colour titrations were specifically developed to replace manual titration. LED illumination ensures constant imaging conditions. The compact industrial inspection cameras reproducibly record the titration process for live video analysis of the region of interest (ROI) within the liquid area on the field of view. The titrator stations are equipped with mixer and reagent addition. Subsequent additions of titration reagents are gravimetrically reported and can be monitored by video analysis. A high precision syringe for titrant addition is operated dynamically under video analysis to perform fast and precise end-point titration. Automated station cleaning cycles reduce maintenance and prevent sample carry-over.


Proprietary titration station.

Space saving overhead mounted Cartesian robotics move sample flasks from one workstation to the next according the protocol and scheduled by **priority**. Loaded samples are tracked throughout the process by their sample **identification**. Workstations are operated by microcontrollers to **autonomously** execute their task based on supplied sample parameters. Returned performance results after each task are logged in the sample database and linked to the sample identification. The **gravimetric control** on every single addition makes each individual step of an analytical method **traceable** and highly **reproducible**. Error trapping, smart retry, recovery with sample abort and automatic aliquot regeneration ensure every entered sample produces a **validated result**.

CENTRAL WEB BASED SOFTWARE

The platform is controlled by **ROBIN**, a real-time event driven **scheduling software** developed by Nucomat. The user-friendly web interface allows the user to run samples, oversee the processes, and get information and timely warnings on addition of fresh reagents. All samples are electronically **tracked** from registration to result and relevant actions are logged to a database. Instrument calibration, control, reference sample analysis and cleaning cycles are automatically managed. Additional process control **business rules** can be implemented. Sample data can be validated online through the web interface and released for reporting, typically to a LIMS system. **Input and reporting** functionality are available with various file formats: text files, RTF, Excel, XML, and reports in PDF.
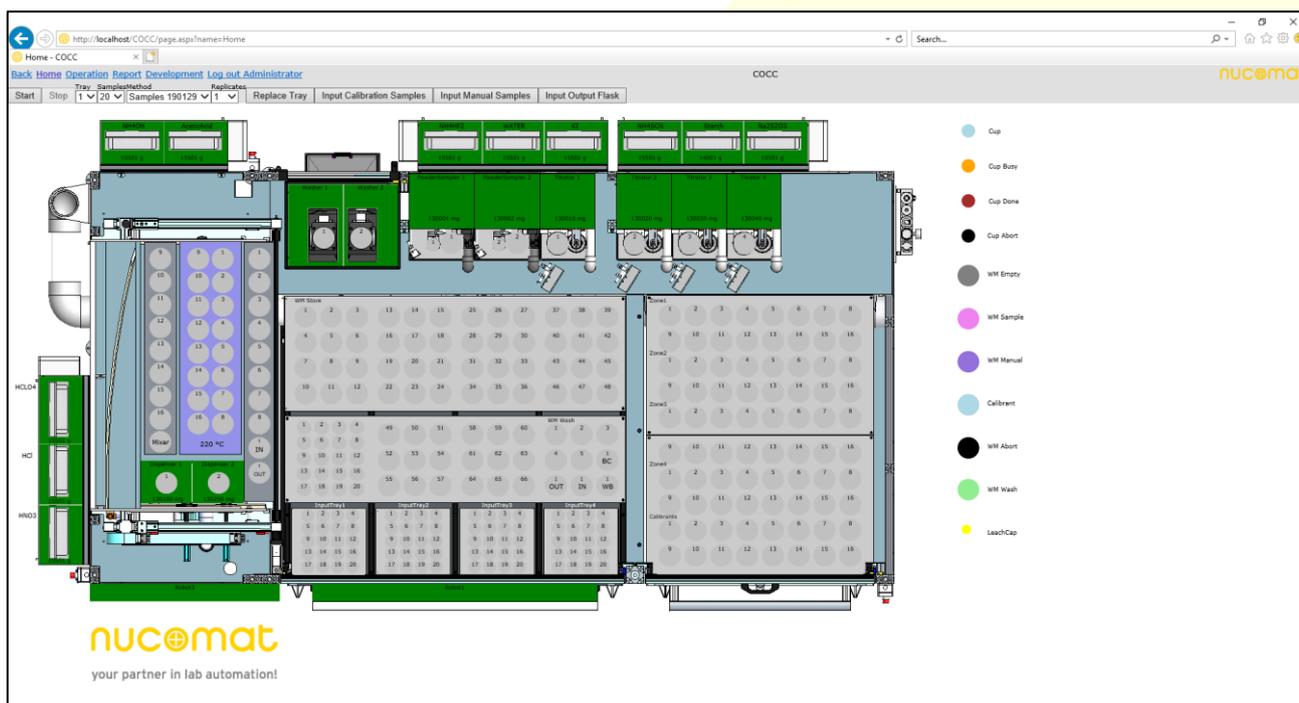

Web based ROBIN software for the copper concentration system

RESULTS

Optimization

Powder sampling optimization: For the pure copper reference 100 mg of powder was dispensed. For the samples with an expected 25% copper content (range 20% to 30%) the powder dispensing was set to 400 mg. When the sample has a copper concentration outside the dynamic range set in the protocol, the equivalence point may not be reached. The sample can be retested using lower sample weight for higher concentrations of copper or a higher sample weight for lower copper concentrations. For this study, the replicates were performed in quadruplicate to allow for statistical comparison. All ore samples were found to be within the dynamic range of 20% to 30% copper and no re-run on different sample weights were needed.
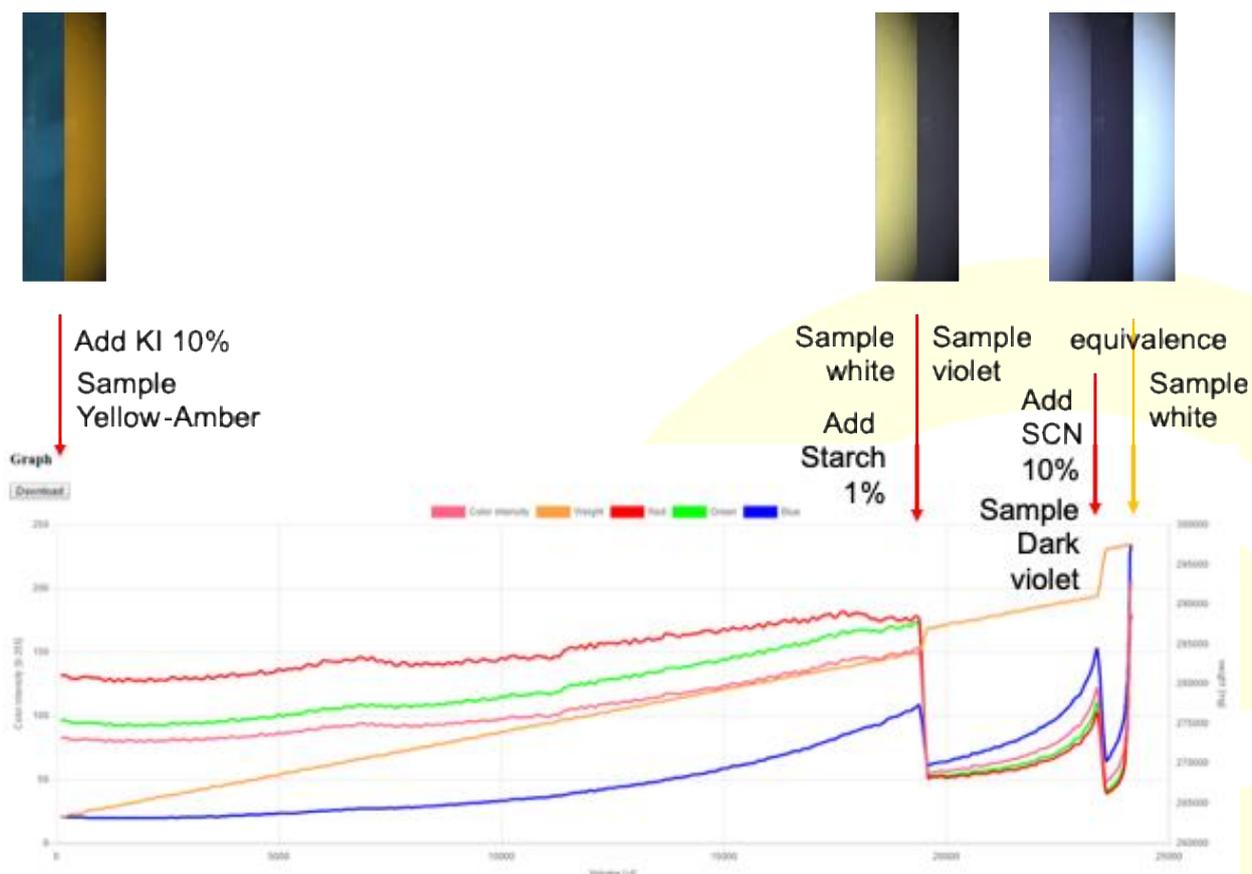
Titrator interface view of an ore sample titration showing colour transition at equivalence in different colour channels
The rectangles on top shows a frame from the video monitor before and after reagent additions. The orange sloped curve shows the weight of the titration flask monitored throughout the titration and used for QC checks on the reagent additions.

To improve smooth operation, care was taken that the subsequent titrator reagent addition points and final equivalence point can be reached within one syringe stroke of the titrant dispenser. To maximise the dynamic range of titration the syringe is reloaded at each reagent addition point. The titrator interface allows to monitor the behaviour of the samples during protocol optimization. In line with the manual approach the colour change in relation to the titration is a good guide for visual inspection of the transition points for titration addition and for end-point equivalence decisions. Please note the illumination, camera settings and influences from coloured components in the sample can affect the outcome of the titration. For the illumination both the intense dark violet samples stages as well as the bright decoloured sample stages need to read within the dynamic range of the camera, as expressed in grey values. On the 3x8-bit RGB camera the dark samples should read near or below 50 grey values, and the bright white samples near 200 grey values for optimal video analysis.

It is useful to test all typical variations of samples from day-to-day practice when optimizing the titrators on installation and preventive maintenance. Check if samples are following the normal titration curve, not interrupted by external factors (such as power spikes or strong variable external light), by incomplete sample preparation or by variations in sample composition and origin. Adjust sample or reagent concentrations or timings to obtain smooth titration curves with sharp equivalence transition.

Typical end-titration curve shapes for refence material (left group) and ore samples (right group).
Variation between replicates is due to small variation in powder weight dispensed for sample preparation.
The weight is accurately recorded to correctly calculate the copper concentration from the titration endpoint.

Wash cycles using diluted titrant in between sample runs are effective to remove any build-up of stain on the stirring bar and dispensing probe heads. With a short wash cycle after each run, carry-over contamination is easily prevented and tedious procedures to remove built up stain are not required. These wash cycles are included in the capacity calculations: While the time from start to equivalence point in titration is sample dependent, typical sample tick rates of 12 to 15 minutes per titrator are achieved. This includes a 1-minute titrator wash step following each titration.

Variability:

Running a variety of ore samples prepared as fine powder, we have demonstrated high precision readout with standard deviations as low as 0.13% on samples having near 28% copper content. When comparing 2 sets of quadruplicate runs on the same sample again the same standard deviation was obtained, and the average sample quantification between the 2 runs was only 0.07% apart. (see table)

Run	sample weighed (mg)	Cu determined (mg)	Cu content %	avg Cu %	stdev Cu %
1	481.5	136.5	28.35%		
	427.6	122.3	28.60%		
	428.1	121.6	28.40%		
	420.4	120.2	28.60%	28.49%	0.13%
2	467.8	134.6	28.78%		
	429.4	121.7	28.34%		
	431.9	123.5	28.58%		
	483.5	137.9	28.52%	28.56%	0.13%

2 runs of the same ore sample performed automatically from powder dispensing of
4 replicate samples, from sample preparation up to completion of titration.

As shown on the plot, the correlation between weight and the titrated amount of copper is highly linear even with quite different weights of powder sampled.

Correlation plot between weight and copper mass titrated, showing strong linear correlation.

For review and auditing purpose, all reagent additions are gravimetrically controlled and logged. This log can be retrieved in the Robin sample list as well as in the reports generated. In case of optimization these data can be a helpful tool. The data are also available for troubleshooting failed samples during routine operation.

Analysis StartTime 23/08/2018 13:48:07	Method Titration 180801 KVD	Status Done	EndTime 23/08/2018 14:57:04			
DateTime	Parameter	Value	Unit	StepNumber		Location
23/08/2018 13:48:07	Sample	425,50	mg	1		Sampler
23/08/2018 13:49:53	HNO3	14.011,00	mg	2		Dispenser
23/08/2018 13:49:53	HCL	5.781,00	mg	2		Dispenser
23/08/2018 13:49:53	HCLO4	5.118,00	mg	2		Dispenser
23/08/2018 14:32:23	Water	24.852,00	mg	9		Dispenser
23/08/2018 14:41:27	NH4OH	4.386,00	mg	12		Dispenser
23/08/2018 14:41:27	NH4HF2	19.833,00	mg	12		Dispenser
23/08/2018 14:47:01	AceticAcid	5.203,00	mg	14		Dispenser
23/08/2018 14:47:01	Water	49.890,00	mg	14		Dispenser
23/08/2018 14:57:04	KI	30.990,00	mg	1		Titrator
23/08/2018 14:57:04	Starch	2.920,00	mg	1		Titrator
23/08/2018 14:57:04	NH4SCH	5.590,00	mg	1		Titrator
23/08/2018 14:57:04	NH2S2O3	23.916,00	µl	1		Titrator
23/08/2018 14:57:04	EquivalencePoint	23.790,00	µl	1		Titrator

Example of a sample report, showing detail of all gravimetric control steps, including time of completion of each step.

COPPER ANALYSIS PROCESS INTEGRATION

The sample preparation and analysis process can be implemented to cover different parts of the procedure. Powder samples can be weighed from powder automatically in replicates, or pre-weighed sample in test flasks can be entered onto the system. After sample preparation samples can be titrated automatically or presented to the user for off-line titration. This allows to flexibly fit the automation into the standard laboratory workflow. And it allows to test and optimise particular steps separately. The database reporting of sample results can be presented for manual download (reports) or linked to a LIMS system.

BENEFITS FOR USERS

- Operator safety
- Traceability and repeatability
- Gravimetric accuracy
- Validated results

TAILOR-MADE SOLUTIONS

Nucomat builds turnkey automated systems based on your requirements (required capacity, type of characterization techniques and ageing protocols, …). Instruments from other manufacturers can also be incorporated in the automated system to expand system specifications.

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